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$GdRuC_2$, a Ternary Carbide with Filled NiAs Structure

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The new carbide $GdRuC_2$ is a high-temperature phase prepared by arc-melting of the elemental components. Its crystal structure was determined from single-crystal X-ray data to be *Cmcm*, a = 436.5(1) pm, b = 927.7(1) pm, c = 520.2(1) pm, Z = 4, and R = 0.015 for 292 structure factors and 16 variable parameters. The unit cell corresponds to the orthorhombic subgroup setting of the hexagonal NiAs structure with Ru and Gd atoms occupying the positions of the Ni and As atoms, respectively. The carbon atoms form pairs with a C–C distance of 137.9(6) pm, and together with the Ru atoms they form two-dimensionally infinite polyanions, where the environment of the Ru atoms seems to be compatible with the 18-electron rule. $GdRuC_2$ is ferromagnetic with a Curie temperature of T_C = 45(3) K and a paramagnetic moment of μ_{exp} = 8.0(1) μ_B. This moment compares well with the free ion value of Gd^{3+} μ_{eff} = 7.94 μ_B, suggesting that the Ru atoms are nonmagnetic.

INTRODUCTION

In recent years a large number of ternary rare earth transition metal carbides have been synthesized (1). With ruthenium as the transition metal component, single carbon atoms have been found in the perovskite-type carbides $ScRu_3C$ (2) and $CeRu_3C$ (3). Carbon pairs occur in Sc_3RuC_4 (4), while single carbon atoms together with carbon pairs are present in $Gd_{12}Ru_{7.5}C_{20}$ (5), $Er_7Ru_2C_{11}$ (6), and $Er_{10}Ru_{10}C_{19}$ (7). With the latter composition a whole series of closely related structures is observed (8), however, all of these—in spite of the similar composition—have entirely different structures than the very simple one reported here for $GdRuC_2$. A preliminary report of the present work was given at a conference (9).

SAMPLE PREPARATION

Starting materials were filings of gadolinium metal, ruthenium powder (both with nominal purity >99.9%), and graphite flakes (>99.5%). Cold-pressed pellets (~0.2 g) were melted in an arc-melting furnace in a purified argon atmosphere. The buttons were turned over and remelted several times to improve their homogeneity. Weight losses, mainly due to the exothermic reaction, were on the order of 3–10%. $GdRuC_2$ was found only in samples which were rapidly quenched from the melt. Samples with a higher weight (~1 g) did not cool fast enough to retain $GdRuC_2$. Such samples contained $Gd_{10}Ru_{10}C_{19}$ (8) and graphite. The same result was obtained when such samples were annealed at temperatures between 900 and 1450°C. $GdRuC_2$ with graphite as a major impurity and traces of $Gd_{10}Ru_{10}C_{19}$ was obtained by arc-melting samples with a higher carbon content (Gd : Ru : C = 1 : 1 : 2.5–3). Similarly $GdRuC_2$ can also be prepared by arc-melting $Gd_{10}Ru_{10}C_{19}$ with an excess of graphite, followed by rapid cooling.

The single crystal of $GdRuC_2$ used for the crystal structure determination was obtained by annealing an arc-melted button in a high-frequency furnace for about 3 h slightly below the melting point. For this purpose the sample was placed in an evacuated and sealed silica tube, which was cooled from the outside with flowing water to minimize the reaction of the sample with the silica.

CHEMICAL PROPERTIES AND LATTICE CONSTANTS

Powdered samples of $GdRuC_2$ are gray and stable in air. Single crystals show metallic luster. The compound does not hydrolyze in water. Energy-dispersive analyses in a scanning electron microscope did not reveal any impurity elements heavier than sodium.

The powder diagrams were indexed on the basis of the orthorhombic cell resulting from the single-crystal investigation. The lattice constants were obtained by different techniques, Guinier powder diagrams and powder diffractometer data refined with the Rietveld technique (10), both with α-quartz (a = 491.30 pm, c = 540.46 pm) as a standard, as well as with high-angle single-crystal diffractometer data. All agreed within three standard deviations. Table 1 lists the weighted averages. Samples prepared with varying starting compositions had the same lattice constants, suggesting a very narrow homogeneity range.

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TABLE 1
Crystallographic Data for $GdRuC_2$

Formula weight	282.3
Space group	*Cmcm* (No. 63)
Lattice constants	a = 436.5(1) pm
	b = 927.7(1) pm
	c = 520.2(1) pm
	V = 0.2107 nm^3
Formula units per cell	Z = 4
Calculated density [g/cm^3]	ρ_{calc} = 8.90
Crystal dimensions [mm]	0.01 · 0.01 · 0.02
Transm. coeff. (highest/lowest)	1.087
$\theta/2\theta$ scans up to	2θ = 80°
Range in h, k, l	±7, ±16, 0–9
Total number of reflections	1414
Internal residual	R_i = 0.022 for 405 averaged data
Data with $I_o > 3\sigma(I_o)$	292
Number of variables	16
Conventional residual	$R(F_o)$ = 0.015
Weighted residual	$R_w(F_o)$ = 0.014

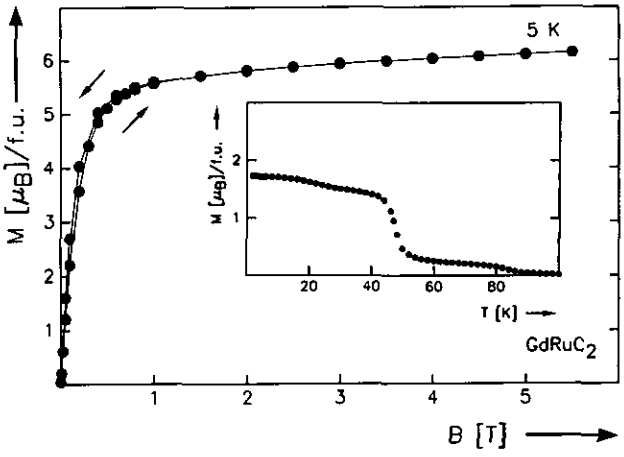

FIG. 2. Magnetization of $GdRuC_2$ as a function of the magnetic flux density measured at a temperature of 5 K. The inset shows the temperature dependence of the magnetization as recorded with a magnetic field strength of 0.1 T.

MAGNETIC PROPERTIES

Susceptibility measurements of a polycrystalline sample of $GdRuC_2$ were carried out with a SQUID magnetometer in the temperature range between 2 and 300 K using magnetic flux densities of up to 5.5 T, as described previously (11, 12). The sample contained a small amount of a ferromagnetic impurity as revealed by the field dependence of the magnetic susceptibility below about 80 K (Fig. 1). However, the susceptibility values measured with flux densities of 3 and 5 T were practically identical. The compound shows Curie–Weiss behavior with a Weiss constant (obtained from the extrapolation of the linear portion of the $1/\chi$ vs T plot above 150 K) of Θ = 38(3) K and a magnetic moment of μ_{exp} = 8.0(1) μ_B. This value agrees well with the moment of μ_{eff} = 7.94 μ_B calculated from the relation $\mu_{exp} = g[J(J+1)]^{1/2}\,\mu_B$ for a Gd^{3+} ion, where g is the Landé factor and J is the total angular momentum quantum number. Thus, the ruthenium–carbon polyanion does not seem to carry a magnetic moment.

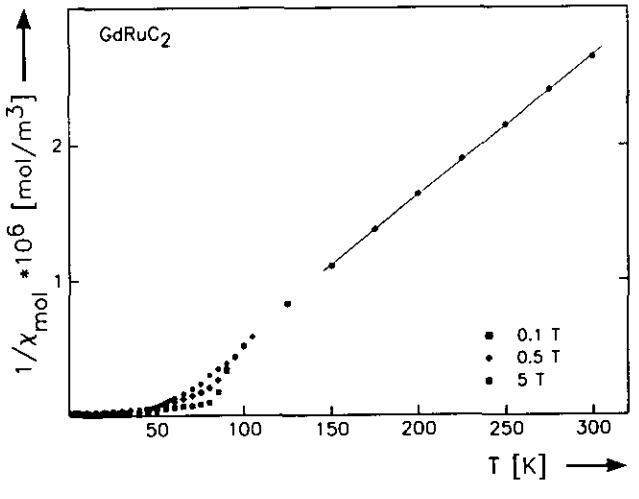

FIG. 1. Reciprocal magnetic susceptibility of $GdRuC_2$ as a function of temperature measured with magnetic flux densities of 0.1, 0.5, and 5 T.

At lower temperatures the reciprocal susceptibility curve approaches zero, suggesting ferromagnetism, which was confirmed by magnetization measurements (Fig. 2). The magnetization curve recorded at 5 K nearly shows saturation already at relatively low magnetic field strengths. A magnetic moment of $\mu_{exp(SM)}$ = 6.1(1) μ_B was calculated from the magnetization measured at 5.5 T. This value may be compared with the theoretical saturation moment of $\mu_{calc(SM)}$ = 7.0 μ_B, calculated according to $\mu_{calc(SM)} = g \cdot J\,\mu_B$. Thus, the experimental value is somewhat smaller than the theoretical one, as could be expected for a powder sample with random orientation of the particles.

The inset of Fig. 2 shows the magnetization behavior as a function of temperature. A Curie temperature of T_C = 45(3) K was estimated from the turning point. The other very weakly pronounced turning point of that curve at about 20 K is due to a minor amount of the impurity $Gd_{10}Ru_{10}C_{19}$ (13). The magnetization behavior as a function of the magnetic field at 5 K shows an unusually small hysteresis. This lack of a pronounced remanence and coercitivity may be attributed at least partially to the fact that the sample was very microcrystalline, not only because it was ground to a powder, but also because it was quenched from high temperature at a very fast rate. In addition, gadolinium ions with a half-filled f shell occa-

sionally show no anistropy and therefore rotate their moments easily.

STRUCTURE DETERMINATION

Single crystals of $GdRuC_2$ were investigated with a Buerger precession camera. The strongest reflections suggested hexagonal symmetry, but the lattice shows a significant orthorhombic distortion. The cell has the extinction conditions for a C-centered lattice and an additional extinction rule for the reflections $h0l$, which were observed only with $l = 2n$. Thus, the space groups *Cmcm*, *C*2*cm*, and $Cmc2_1$ were possible. The structure determination resulted in the centrosymmetric group *Cmcm*.

Intensity data were collected within one half of the reciprocal space in a four-circle diffractometer (CAD4) with graphite-monochromated Mo$K\alpha$ radiation and a scintillation counter with a pulse-height discriminator. Background counts were recorded at both ends of each $\theta/2\theta$ scan. An empirical absorption correction based on psi scan data was applied. Further details of the data collection are given in Table 1.

The positions of the metal atoms were found by interpretation of the Patterson function; the carbon site was located through a difference Fourier synthesis. The structure was refined by full-matrix least-squares cycles. The atomic scattering factors (14) were corrected for anomalous dispersion (15). The weighting scheme was based on the counting statistics and a factor correcting for secondary extinction was refined and applied to the calculated structure factors. To check for deviations from the ideal composition, occupancy factors and anisotropic thermal parameters were refined simultaneously in separate least-squares cycles while the scale factor was held constant. Since all sites are fully occupied within three standard deviations (Table 2) the ideal composition was assumed for the last cycles. A final difference Fourier synthesis gave the highest peak with 0.88×10^3 e/nm^3, too close to the ruthenium site and too low for additional atomic sites when compared with the peak height of 11.9×10^3 e/nm^3 for a carbon atom. The structure factor tables have been recorded in (16).

TABLE 2
Atomic Parameters for $GdRuC_2$[a]

Atom	Gd	Ru	C
Cmcm	4*c*	4*b*	8*g*
Occup.	1.002(1)	0.994(2)	1.03(1)
x	0	0	0.158(1)
y	0.18295(3)	0.5	0.9130(4)
z	¼	0	¼
U(11)	55(1)	39(2)	80(16)
U(22)	35.7(9)	62(2)	69(14)
U(33)	62.4(9)	34(1)	45(12)
U(12)	0	0	9(14)
U(13)	0	0	0
U(23)	0	6(1)	0
B_{eq}	0.403(4)	0.355(6)	0.51(6)

[a] Numbers in parentheses are estimated standard deviations in the place values of the least significant digits throughout the paper. The anisotropic thermal parameters U in units of pm^2 are defined as $U_{hkl} = \exp\{-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{23}klb^*c^*)\}$. The last row contains the equivalent isotropic B values ($\times 100$, in units of nm^2). The occupancy parameters were varied in separate least-squares cycles together with anisotropic displacement parameters of all atoms. In the final least-squares cycles all atomic sites were assumed to be fully occupied.

DISCUSSION

The structure of $GdRuC_2$ (Fig. 3) is of a new, relatively simple type, which may be derived from the NiAs type structure. The gadolinium atoms form a (distorted) close-packed hexagonal arrangement with the ruthenium atoms filling the octahedral voids. Thus, the gadolinium and ruthenium atoms correspond to the arsenic and nickel atoms of NiAs. The carbon atoms form pairs, which fill the trigonal bipyramidal voids formed by the gadolinium atoms, and in that sense the structure of $GdRuC_2$ corresponds to the filled NiAs structure of Ni_2In. The C–C bond of the carbon pairs is oriented perpendicular to the trigonal axis of the trigonal bipyramid of the gadolinium atoms.

The gadolinium atoms are each surrounded by eight carbon atoms, six ruthenium atoms, and four gadolinium atoms. Thus, they each have 18 near neighbors. Of these, the four gadolinium neighbors are certainly only weakly

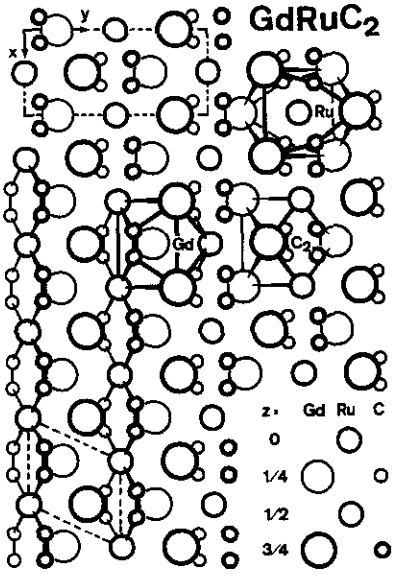

FIG. 3. Crystal structure and coordination polyhedra of $GdRuC_2$. In the upper left-hand corner the orthorhombic cell is outlined; in the lower left-hand corner the hexagonal subcell corresponding to the NiAs structure is shown. On the left side the ruthenium and carbon atoms are connected to emphasize the two-dimensionally infinite polyanion.

TABLE 3
Interatomic Distances in $GdRuC_2$[a]

Gd: 2 C 259.8(4)	Ru: 4 C 213.8(4)	C: 1 C 137.9(6)
2 C 260.5(4)	2 Ru 260.1(1)	2 Ru 213.8(4)
4 C 283.4(2)	4 Gd 305.5(1)	1 Gd 259.8(4)
4 Ru 305.5(1)	2 Gd 321.6(1)	1 Gd 260.5(4)
2 Ru 321.6(1)		2 Gd 283.4(2)
4 Gd 361.6(1)		

[a] All distances shorter than 420 pm (Gd–Gd, Gd–Ru, Ru–Ru), 320 pm (Gd–C and Ru–C), and 298 pm (C–C) are listed.

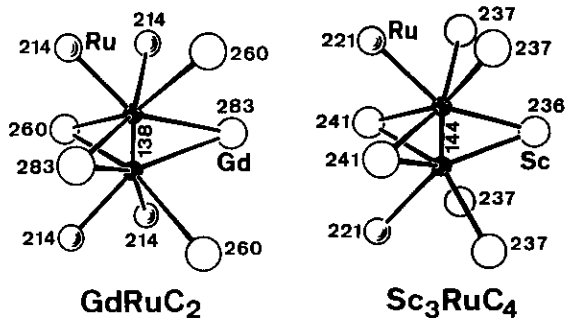

FIG. 4. The coordination of a C_2 pair in $GdRuC_2$ as compared to that in the Sc_3CoC_4-type structure of Sc_3RuC_4. Interatomic distances are indicated in pm units.

bonded, even though the Gd–Gd distances of 361.6 pm (Table 3) compare well with the distance of 360.4 pm obtained by doubling the metallic radius of gadolinium for the coordination number 12 (17). Gadolinium is the most electropositive component of the compound and therefore the gadolinium atoms have mostly donated their valence electrons to the ruthenium and carbon atoms. A comparison of the Gd–C distances in $GdRuC_2$ and $Gd_3Mn_2C_6$ (18) is of interest. In both compounds the gadolinium atoms have eight carbon neighbors. However, the average Gd–C distances of 271.8 pm in $GdRuC_2$ and 263.4 pm in $Gd_3Mn_2C_6$ are remarkably different. This can be rationalized if the Gd–Ru interactions of $GdRuC_2$ are considered as bonding, because the four short Gd–Ru distances of 305.5 pm in $GdRuC_2$ are shorter than the shortest Gd–Mn distances of 307.4 pm (1×) and 314.6 pm (2×) in $Gd_3Mn_2C_6$, even though the metallic radius of the ruthenium atoms is about 6 pm greater than the radius of a manganese atom for the coordination number 12.

The ruthenium atoms in $GdRuC_2$ are coordinated by a distorted octahedron of gadolinium atoms. The distortion arises mainly through two close ruthenium atoms, which are situated outside two opposite triangular faces of the octahedron. The coordination is completed by four carbon neighbors, which are located approximately at the edges of the octahedron formed by the gadolinium atoms.

The carbon atoms are paired with a C–C distance of 137.9(6) pm, which is slightly greater than the double-bond distance of 135 pm found in olefins. The C_2 pair is located in a trigonal prism formed by four ruthenium and two gadolinium atoms with three additional gadolinium atoms outside the rectangular faces of the prism. This coordination is somewhat similar to that found for the carbon atoms in Sc_3RuC_4 (4). However, there the carbon pairs have two ruthenium and seven gadolinium neighbors (Fig. 4). Alternatively, the coordination of the C_2 pair may be described as derived from a trigonal bipyramid of gadolinium atoms as already mentioned above.

Together with the ruthenium atoms, the carbon pairs of $GdRuC_2$ form a two-dimensionally infinite polyanion $(RuC_2)_n$ (Fig. 5) with a formal charge of −3 per RuC_2 unit. Considering that the C–C distance corresponds to a double bond, the formula may be written $Gd^{+3}Ru^{+1}(C_2)^{-4}$, where the superscripts are oxidation numbers (formal charges), i.e., the ruthenium atoms do not need to carry magnetic moments, because they form Ru–Ru bonds. Actually it may be argued that the ruthenium atoms obey the 18-electron rule. A plausible valence electron distribution using the Lewis formalism is outlined in Fig. 6. In this scheme each ruthenium atom accommodates 18 electrons: eight in the four bonds to the carbon atoms, six in the two bonds to the neighboring ruthenium atoms, and four nonbonding electrons, shown as dots near the ruthenium atoms. It can also be seen that the carbon atoms follow the octet rule. In the ascription of oxidation numbers the valence electrons of the Ru–C bonds are *counted* at the carbon atoms and the electrons of the Ru–Ru bonds are "split" between the ruthenium atoms. Thus, each ruthenium atom obtains three electrons from the Ru–Ru bonds,

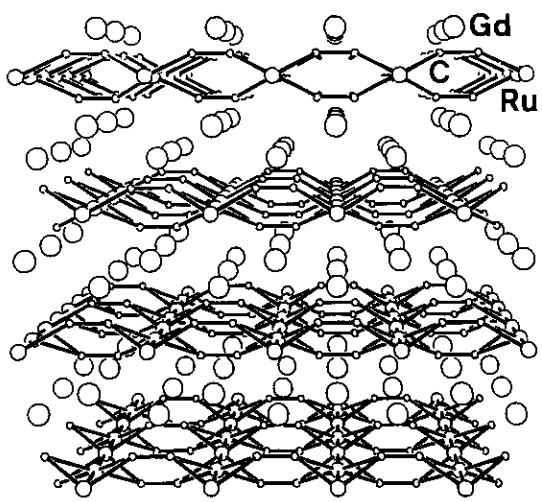

FIG. 5. Perspective view of the $GdRuC_2$ structure emphasizing the two-dimensionally infinite ruthenium–carbon polyanions.

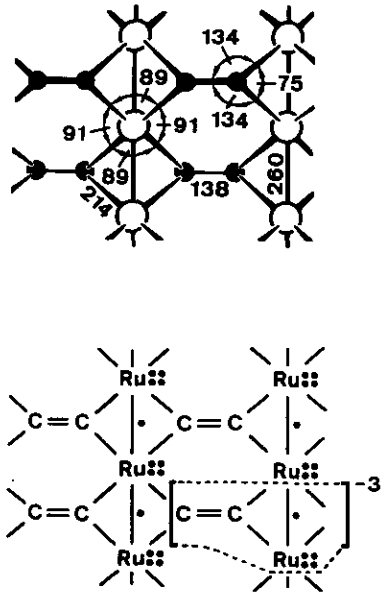

FIG. 6. A cutout of the two-dimensionally infinite polyanion $[RuC_2]_n^{-3n}$. In the upper part interatomic distances [pm] and angles [°] are indicated. In the lower part the Lewis formalism is used to show the valence electron distribution assuming the 18- and 8-electron rules for the ruthenium and the carbon atoms are obeyed.

which together with the four nonbonding electrons form the so-called d^7 system. The 18-electron rule is well established in organometallic chemistry and we believe that it should also be valid for most solid state compounds. Obviously this rationalization of chemical bonding is very crude; nevertheless it is somewhat supported by a comparison of bond lengths. For instance, in $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ (19), the Ru–C bonds have a bond order of one, and the Ru–C distances of between 210.3(6) pm and 211.2(4) pm in that compound are similar to the Ru–C distance of 213.8(3) pm in $GdRuC_2$. Also, the Ru–Ru distance of 265.0(1) pm in the organometallic compound is greater than the Ru–Ru distance of 260.1(1) pm in $GdRuC_2$. Hursthouse *et al.* (19) ascribe a bond order of one to the Ru–Ru interactions of that diamagnetic compound (although then the ruthenium atoms obtain only 17 electrons), which compares rather well with the bond order of 3/2 assumed by us for the Ru–Ru bonds in $GdRuC_2$.

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