The Rare Earth Carbides R_4C_5 with R = Y, Gd, Tb, Dy, and Ho

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The five carbides R_4C_5 (R = Y, Gd–Ho) have been prepared by arc-melting cold-pressed pellets of the elemental components and subsequent annealing at 1050°C. They crystallize with a new orthorhombic structure type (*Pbam, Z* = 2), which has been determined from X-ray powder diffractometer data of Y_4C_5 (a = 657.35(9) pm, b = 1191.8(1) pm, c = 366.92(5) pm, R_F = 0.035 for 179 structure factors) and also refined from powder data of Tb_4C_5 (a = 660.8(1) pm, b = 1197.3(2) pm, c = 368.71(6) pm, R_F = 0.035 for 181 F values) and Ho_4C_5 (a = 653.00(8) pm, b = 1184.6(1) pm, c = 363.80(4) pm, R_F = 0.036 for 171 F values and 10 positional parameters each). The structure contains building blocks, which were also found in the two closely related structures of α- and β-Ho_4C_7. One-fifth of the carbon atoms are isolated from each other and coordinated octahedrally by rare earth atoms. The other carbon atoms form pairs with C–C bond distances of 133.5(15), 136(3), and 129(2) pm in Y_4C_5, Tb_4C_5, and Ho_4C_5, respectively, corresponding to C–C double bonds. Hence, all valence electrons can be accommodated in bonding R–C and C–C states according to the formula $(R^{+3})_4(C_2^{-4})_2C^{-4}$, where the superscripts represent oxidation numbers. Nevertheless, the hydrolyses of Y_4C_5 and Ho_4C_5 with distilled water resulted in up to 41 wt% ethane, up to 16 wt% propane and propene, and up to 18 wt% higher hydrocarbons in addition to the expected products methane and ethylene.

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INTRODUCTION

Several binary carbides of scandium, yttrium, and the heavy lanthanoids with high carbon content have been characterized in recent years. The carbides R_3C_4 (R = Sc, Ho–Lu) crystallize with a structure, which has been determined from single-crystal X-ray data of the scandium compound (1). More recently the isotypic carbides Y_4C_7 and Ho_4C_7 were reported. Their structure was determined from single-crystal X-ray data of Ho_4C_7 (2). The latter compound is stable at relatively low temperatures. It was subsequently designated as the α-phase, since a high-temperature (β-) modification with this composition was also found. The latter is isotypic with the carbides R_4C_7 (R = Er, Tm, and Lu). Their structure was determined from X-ray powder data of the holmium and neutron powder data of the lutetium compound (3).

Here we report on another series of binary rare earth carbides. The yttrium compound has already been characterized earlier by its d spacings, and it has been assigned the tentative composition ∼ Y_5C_6 (4). Subsequently ∼ Ho_5C_6 was established to be isotypic with ∼ Y_5C_6 on the basis of its similar X-ray powder pattern (5). In the present article we report the crystal structure of these carbides, which we find to have the compositions Y_4C_5 and Ho_4C_5. Preliminary results of this work have been presented at a conference (6).

SAMPLE PREPARATION, LATTICE CONSTANTS, AND HYDROLYSES

Starting materials were ingots of rare earth metals, all with nominal purities > 99.9%, and graphite flakes (Alpha, > 99.5%). Filings of the rare earth elements were prepared under paraffin oil. The oil was removed by *n*-hexane. Because of its reactivity, the filings of yttrium had to be stored under vacuum. The carbides were prepared by arc-melting small (∼ 400 mg) cold-pressed pellets of the elemental components with the atomic ratio R:C = 48:52 in an atmosphere of argon (> 99.996%). The starting R:C ratio was slightly off the ideal composition 4:5 on purpose, because we preferred to have the face-centered cubic carbides R_3C as impurities, rather than the carbides with a higher carbon content, which have complex powder patterns. A titanium button was melted at least three times prior to the reactions to enhance the purity of the argon atmosphere. The samples were melted from both sides to enhance their homogeneity. They were then wrapped in tantalum foil and annealed in evacuated silica tubes for 40 days at 1050°C. The sample tubes were crushed in a drybox under nitrogen (oxygen content < 0.8 ppm) and ground to a fine powder under a protective cover of dried paraffin oil.

Guinier powder diagrams of the samples were recorded with $CuK\alpha_1$ radiation and α-quartz (a = 491.30 pm, c = 540.46 pm) as an internal standard. The compounds

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TABLE 1
Lattice Constants of Carbides with the Orthorhombic Y_4C_5 Type Structure[a]

Compound	a (pm)	b (pm)	c (pm)	V (nm^3)
Y_4C_5	657.35(9)	1191.8(1)	366.92(5)	0.2875
Gd_4C_5	666.7(1)	1208.4(2)	372.59(8)	0.3002
Tb_4C_5	660.8(1)	1197.3(2)	368.71(6)	0.2917
Dy_4C_5	657.4(1)	1190.5(1)	366.54(5)	0.2869
Ho_4C_5	653.00(8)	1184.6(1)	363.80(4)	0.2814

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

R_4C_5 were not present in the arc-melted, crushed buttons; they are formed during the annealing. Indices for the powder patterns of the carbides R_4C_5 could be assigned on the basis of an orthorhombic cell found with the aid of a computer program (7). The identification of the diffraction lines was facilitated by intensity calculations (8) using the positional parameters of the refined structure. The lattice constants, obtained by least-squares fits, are listed in Table 1. The cell volumes (Fig. 1) reflect the lanthanoid contraction.

Compact samples, but especially powdered samples are very sensitive to the humidity of the air. Two samples of Y_4C_5 and a sample of Ho_4C_5 were hydrolyzed with distilled water at room temperature. The gaseous reaction products were fractionized in a gas chromatograph and immediately thereafter analyzed by a mass spectrometer. The results are summarized in Table 2.

STRUCTURE DETERMINATION AND REFINEMENTS

The crystal structure of the five isotypic carbides was determined and refined from X-ray powder diffractometer data of the three compounds Y_4C_5, Tb_4C_5, and Ho_4C_5. Since these carbides are very sensitive to the humidity of the air, the ingots were ground to a fine powder in a glove box

under dried nitrogen. To minimize absorption, powder of α-quartz was added as a diluent. These mixtures were filled into silica tubes with an outer diameter of 0.1 mm, using ultrasonic sound agitation.

The X-ray intensity data (Fig. 2) were recorded from rotating samples on a focusing powder diffractometer
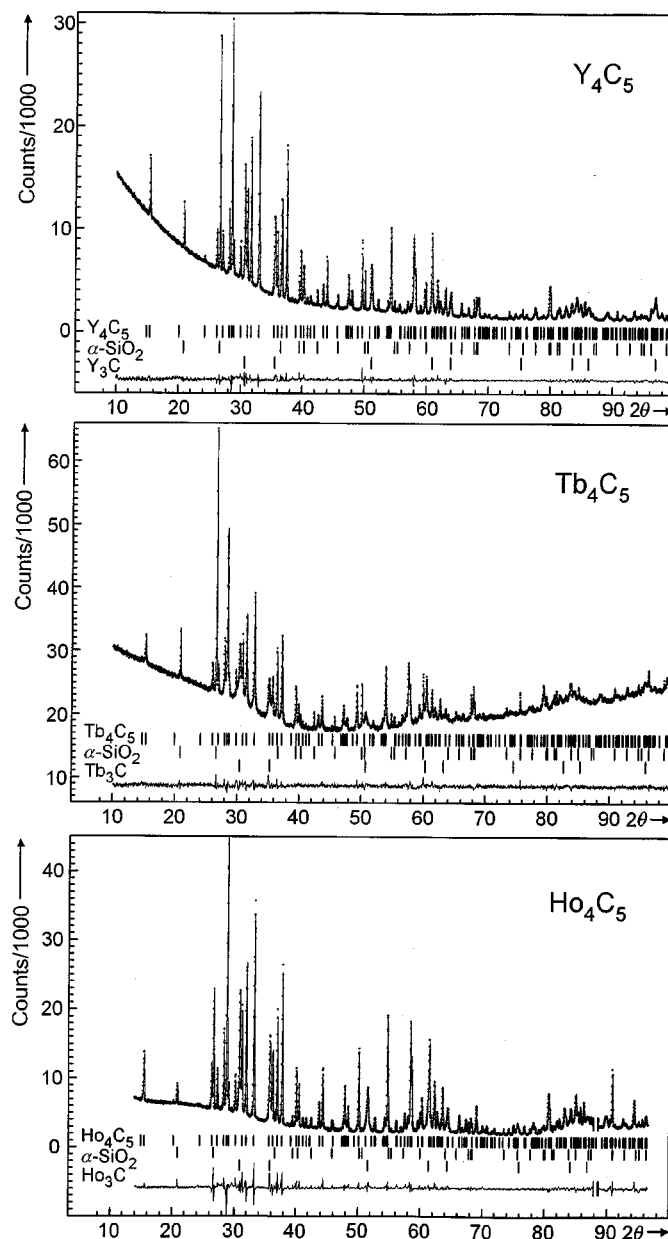

FIG. 2. Rietveld refinement plots for Y_4C_5, Tb_4C_5, and Ho_4C_5. In the uppermost parts of the plots the measured intensity values are indicated by dots and the calculated fits by lines. The peak positions of the carbides, the diluent α-quartz, and the impurity phases R_3C are indicated. The difference profiles between the calculated and the observed plots are also shown.
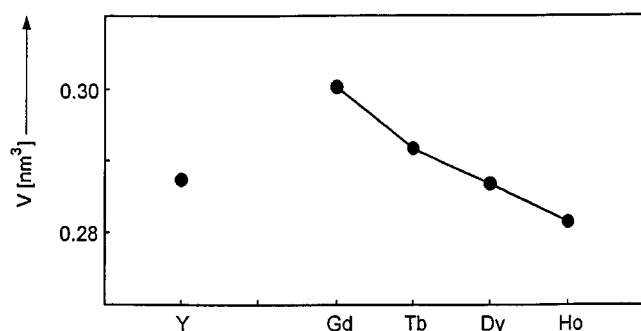

FIG. 1. Cell volumes of the Y_4C_5-type carbides.

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TABLE 2
Results of the Hydrolyses of Y_4C_5 and Ho_4C_5[a]

Reaction product	Y_4C_5 (1)	Y_4C_5 (2)	Ho_4C_5
CH_4	21.5	24.1	42.3
$CH_3 \cdot CH_3$	40.0	41.0	29.6
$CH_2 \cdot CH_2$	5.7	5.0	4.7
$CH \cdot CH$	3.0	1.6	—
$CH_3 \cdot CH_2 \cdot CH_3$	7.0	6.0	8.2
$CH_3 \cdot CH \cdot CH_2$	4.7	5.7	8.0
$> C_3$	18.2	16.7	7.2

[a] Two samples of Y_4C_5 were hydrolyzed. The amounts of the hydrocarbons are listed in wt%.

TABLE 3
Crystallographic Data for Y_4C_5, Tb_4C_5, and Ho_4C_5

Compound	Y_4C_5	Tb_4C_5	Ho_4C_5
Lattice constants	Table 1	Table 1	Table 1
Formula units/cell	2	2	2
Space group	*Pbam* (No. 55)	*Pbam* (No. 55)	*Pbam* (No. 55)
Formula mass	415.68	695.76	719.78
Calculated density (g/cm³)	4.801	7.922	8.495
Range in 2θ (°)	10–100	10–100	13–100
Step width in 2θ (°)	0.02	0.02	0.02
Total measuring time (h)	120	250	98
Total number of steps	4501	4501	4193
Number of reflections	179	181	171
No. of structural parameters	10	10	10
Goodness of fit (χ^2)	3.08	2.18	8.69
Bragg residual	$R_{Bragg} = 0.040$	$R_{Bragg} = 0.044$	$R_{Bragg} = 0.044$
Conventional residual	$R_F = 0.035$	$R_F = 0.036$	$R_F = 0.036$

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(STOE Stadi P) with monochromated $CuK\alpha_1$ radiation, using a linear position-sensitive detector in Debye-Scherrer geometry. Further details of the data collection and the structure refinements are summarized in Table 3.

The structure was solved independently from the powder data of both Y_4C_5 and Ho_4C_5. Intensity data were extracted from the diffractometer scans and Patterson syntheses were computed with the SHELXS-86 single-crystal program system (9). These yielded the positions of several rare earth atoms. The positions of the other rare earth atoms were then obtained after least-squares refinements and difference Fourier calculations using the program package SHELXL-93 (10). With these positions the powder diffractometer data

were refined with the program FULLPROF (11). Subsequent difference Fourier analyses were then calculated using again the single-crystal program systems. Some possible carbon positions were obtained from these calculations. Eventually the positions of all atoms were located and optimized by iteration between the single-crystal refinement and the Rietveld refinement programs. The lattice constants of the impurity phases Y_3C, Tb_3C, and Ho_3C (12) as well as those of the diluent α-quartz were also refined. The intensities of the carbides Y_4C_5, Tb_4C_5, and Ho_4C_5 amounted to 73.3, 69.8, and 75.5%, respectively, of the total sample. In the final Rietveld refinements a total of 33 parameters were optimized for each diffractogram, including the
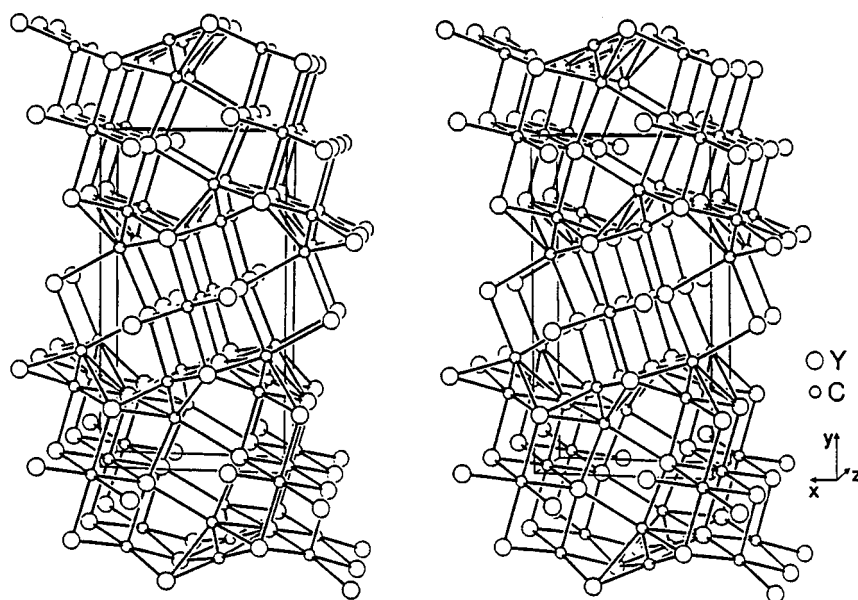

FIG. 3. Stereoplot of the Y_4C_5 structure.

TABLE 4
Atomic Parameters of Y_4C_5, Tb_4C_5, and $Ho_4C_5{}^a$

Atom	Pbam	x	y	z	B
			Y_4C_5		
Y1	4h	0.3922(2)	0.3045(1)	1/2	0.74(3)
Y2	4g	0.2455(2)	0.0434(1)	0	0.73(3)
C1	4g	0.093(2)	0.3443(9)	0	0.6
C2	4g	0.140(2)	0.2353(9)	0	0.6
C3	2b	0	0	1/2	0.6
			Tb_4C_5		
Tb1	4h	0.3920(2)	0.3032(2)	1/2	0.68(5)
Tb2	4g	0.2450(3)	0.0432(2)	0	0.84(5)
C1	4g	0.096(4)	0.341(2)	0	0.6
C2	4g	0.151(3)	0.232(2)	0	0.6
C3	2b	0	0	1/2	0.6
			Ho_4C_5		
Ho1	4h	0.3921(2)	0.3039(1)	1/2	0.52(3)
Ho2	4g	0.2457(3)	0.0437(1)	0	0.83(3)
C1	4g	0.104(3)	0.345(1)	0	0.6
C2	4g	0.143(3)	0.238(1)	0	0.6
C3	2b	0	0	1/2	0.6

^{a} The last column contains the isotropic thermal parameters ($\times 10^4$, in units of pm^2) of the metal atoms. The corresponding parameters of the carbon atoms were held at the indicated values in all refinements.

zero point, two scale factors, all lattice constants, two asymmetry parameters, and for each phase four parameters to fit the peak profiles with pseudo-Voigt functions. The positional parameters of the three carbides and the isotropic displacement parameters of the rare earth atoms could be refined independently, while the displacement parameters of the carbon atoms were held constant at 0.6×10^{-4} pm^2 (Table 4). The number of reflections resulting from the Y_4C_5-type carbides are listed in Table 3. In addition 60 reflections of α-quartz and 9 of the cubic R_3C phase were fitted. The interatomic distances are listed in Table 5, a stereoplot of the structure is shown in Fig. 3, and the coordination polyhedra are presented in Fig. 4.

DISCUSSION

The five carbides R_4C_5 (R = Y, Gd, Tb, Dy, and Ho) crystallize with a new structure type, which we have determined and refined entirely from X-ray powder data of Y_4C_5, Tb_4C_5, and Ho_4C_5. The determination of a new structure type from powder data is now occasionally denoted with the high-flown expression *ab initio*, although this has already been a frequently used procedure before single-crystal diffractometers became available. The positional parameters of Y_4C_5 are the most accurate and for that reason we will refer to this structure to be of the Y_4C_5 type.

TABLE 5
Interatomic Distances in the Structures of Y_4C_5, Tb_4C_5, and $Ho_4C_5{}^a$

		Y_4C_5	Tb_4C_5	Ho_4C_5
R1:	1C3	243.5(1)	246.2(2)	242.8(1)
	2C2	250.0(7)	255(1)	250(1)
	2C2	260.5(8)	258(1)	256(1)
	2C1	273.0(9)	272(2)	266(1)
	2C1	287.4(9)	287(2)	289(1)
	2R2	347.0(2)	349.6(3)	345.0(2)
	2R2	350.6(2)	353.2(3)	349.1(2)
	2R1	353.4(2)	354.1(2)	350.6(2)
	2R1	366.92(5)	368.71(6)	363.80(4)
	2R2	373.9(2)	374.6(3)	370.5(2)
R2:	1C2	239(1)	234(2)	240(2)
	2C3	249.7(1)	250.7(2)	248.0(1)
	1C1	260(1)	264(2)	255(2)
	1C1	265(1)	270(2)	268(2)
	1R2	338.9(2)	339.9(3)	337.2(3)
	2R1	347.0(2)	349.6(3)	345.0(2)
	1R2	350.2(2)	352.6(3)	347.9(3)
	2R1	350.6(2)	353.2(3)	349.1(2)
	2R2	366.92(5)	368.71(6)	363.80(4)
	2R1	373.9(2)	374.6(3)	370.5(2)
C1:	1C2	133.5(15)	136(3)	129(2)
	1R2	260(1)	264(2)	255(2)
	1R2	265(1)	270(2)	268(2)
	2R1	273.0(9)	272(2)	266(1)
	2R1	287.4(9)	287(2)	289(1)
C2:	1C1	133.5(15)	136(3)	129(2)
	1R2	239(1)	234(2)	240(2)
	2R1	250.0(7)	255(1)	250(1)
	2R1	260.5(8)	258(1)	256(1)
C3:	2R1	243.5(1)	246.2(2)	242.8(1)
	4R2	249.7(1)	250.7(2)	248.0(1)

^{a} All distances shorter than 480 pm (metal–metal), 360 pm (metal–C), and 310 pm (C–C) are listed.

As can be seen from Fig. 5 the structure of Y_4C_5 shows similarities with the structures of α-Ho_4C_7 (2) and β-Ho_4C_7 (3). Both modifications of Ho_4C_7 contain single carbon atoms and C_3 units derived from propadiene. In the Y_4C_5-type carbides, single carbon atoms and C_2 units are present. In all three structures the isolated carbon atoms are situated in octahedra formed by the rare earth atoms, and these octahedra share most of their edges with adjacent octahedra, as is known for the NaCl-type structure. The NaCl-type structure is very common for the carbides of the elements in this part of the periodic system, e.g., the extremely stable, technically important carbides TiC, ZrC, HfC, VC,
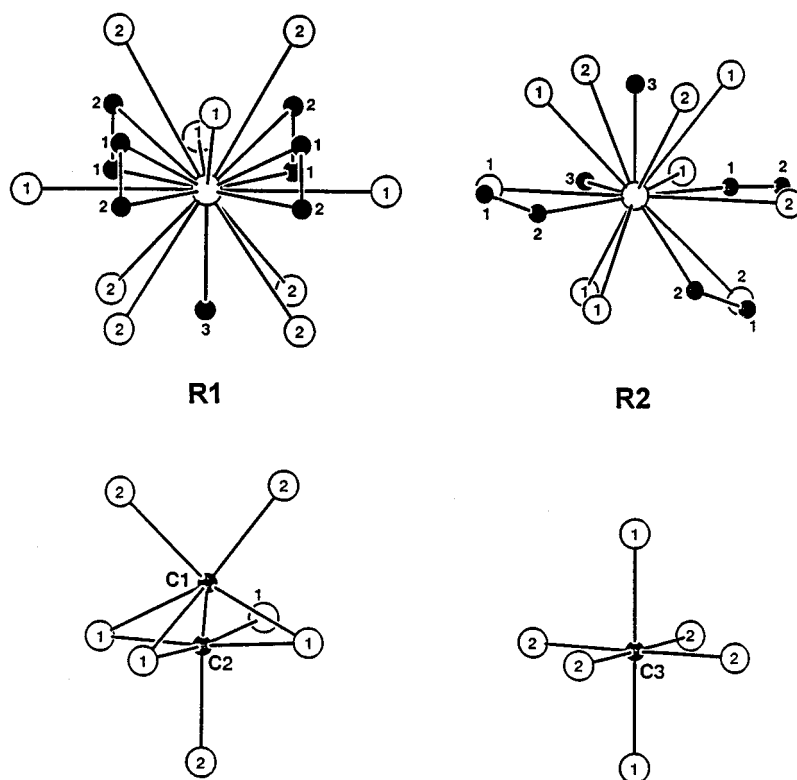
FIG. 4. Near-neighbor environments in the structure of Y_4C_5.

NbC, and TaC have this atomic arrangement. Also NaCl-type building blocks have been recognized in the structures of Sc_3C_4 (1) and $Sc_5Re_2C_7$ (13). In Fig. 5 these NaCl-type building blocks are emphasized by shading.

The $R1$ atoms in the Y_4C_5-type carbides are coordinated by nine carbon and 10 rare earth atoms, while the $R2$ atoms have five carbon and again 10 rare earth metal neighbors. The higher number of carbon neighbors of the $R1$ atoms is reflected by the larger average $R1$–C distances of 265.0, 265.6, and 262.8 pm for the yttrium, terbium and holmium compounds, respectively, as compared to the corresponding average $R2$–C distances of 252.7, 253.9, and 252.0 pm. While the carbon pairs in the environment of the $R1$ atoms are all connected to the central $R1$ atom side-on, they are connected to the $R2$ atom end-on (Fig. 4). The R–R distances of the three compounds cover the relatively narrow range between 337.3 pm (Ho2–Ho2) and 374.6 pm (Tb1–Tb2).

The C_2 units in the three carbides are situated in a void formed by seven rare earth atoms. The arrangement of these seven rare earth atoms may be described as an octahedron, where one corner atom is substituted by two. The C–C bond distances in Y_4C_5, Tb_4C_5, and Ho_4C_5 are 133.5(15), 136(3), and 129(2) pm. The average distance of 132.8 pm is comparable to the C–C bond distance of 134 pm in olefins. Hence,

the C_2 units can be regarded as derived from ethylene, and accordingly they may be assigned an oxidation number of -4; the same number is also appropriate for the isolated C3 atoms. Therefore, these carbides can be rationalized in a first approximation with the formula $(R1^{+3})_2(R2^{+3})_2$ $[(C1$–$C2)^{-4}]_2C3^{-4}$. This does not necessarily mean that these carbides are semiconductors, since the band gap may be closed ("semimetal"). Nevertheless, the structurally closely related carbide Y_4C_7 is semiconducting (2). Its α-Ho_4C_7-type structure contains C_3 units derived from propadiene, and this compound can also be rationalized with oxidation numbers according to the formula $(Y^{+3})_4(C_3^{-4})_2C^{-4}$. In contrast, Sc_3C_4 contains electrons (six for the total cell content of 10 formula units), which cannot be accommodated in Sc–C and C–C bonds, if the octet rule is to be obeyed for the carbon atoms, and consequently it is a metallic conductor (1, 14).

The hydrolysis results of the two samples of Y_4C_5 are very similar (Table 2). This demonstrates their reproducibility. The structure determination showed that 80% of the carbon atoms form pairs with a C–C distance corresponding to a double bond, while the remaining carbon atoms are isolated from each other. Hence, one could expect that about 78 wt% of the reaction products would be ethylene.
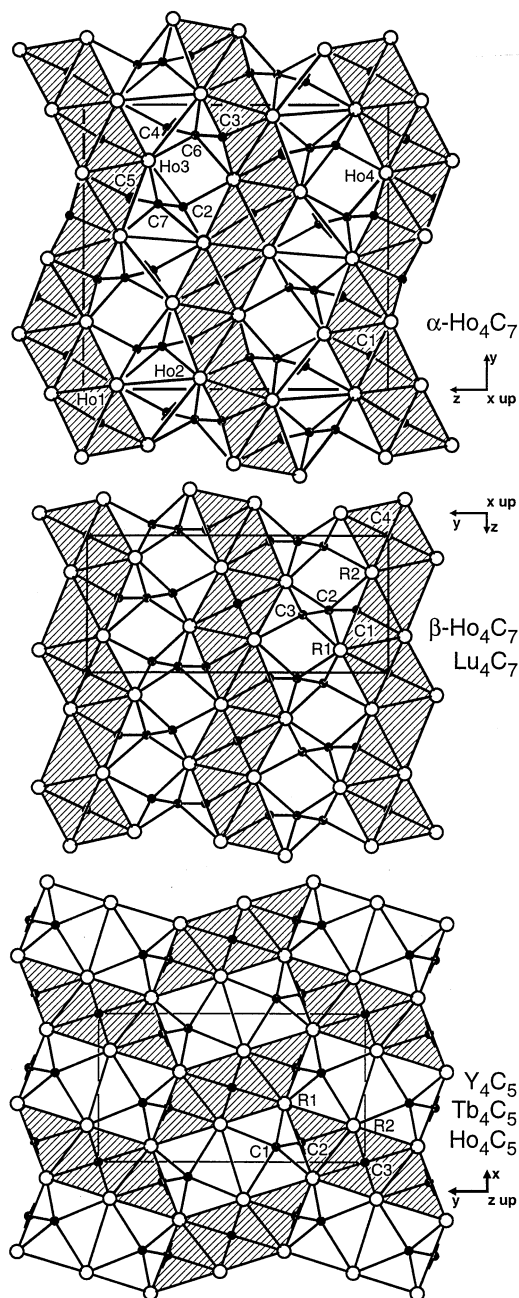
FIG. 5. The crystal structure of Y_4C_5 as compared to the closely related structures of α-Ho_4C_7 and the Lu_4C_7-type structure of β-Ho_4C_7. The three structures are projected along the short translation period, and all atoms are shown. The shaded parts of the structures have atomic arrangements similar to that of NaCl: single carbon atoms are situated in octahedra formed by the rare earth atoms and these octahedra share edges.

However, this is not the case, as is usually observed for binary and ternary rare earth carbides (3, 15, 16). Only Al_4C_3 and CaC_2 yield the expected products methane and acetylene, respectively. Mg_2C_3 produces mainly propyne instead of the expected propadiene (17, 18), while the carbides of the rare earth elements usually produce a great variety of hydrocarbons including products with more than three carbon atoms (3, 15, 16). Lu_4C_7 is an exception probably because the filled f shell may be important in the transition states of the reaction kinetics (3).

ACKNOWLEDGMENTS

REFERENCES

1. R. Pöttgen and W. Jeitschko, *Inorg. Chem.* **30,** 427 (1991).
2. H. Mattausch, T. Gulden, R. K. Kremer, J. Horakh, and A. Simon, *Z. Naturforsch. B* **49,** 1439 (1994).
3. R. Czekalla, W. Jeitschko, R.-D. Hoffmann, and H. Rabeneck, *Z. Naturforsch. B* **51,** 646 (1996).
4. E. K. Storms, *High Temp. Sci.* **3,** 99 (1971).
5. J. Bauer and D. Ansel, *J. Less-Common Met.* **109,** L9 (1985).
6. R. Czekalla, R.-D. Hoffmann, Th. Hüfken, R. Pöttgen, and W. Jeitschko, *Z. Kristallogr. Suppl.* **10,** 96 (1995).
7. J. W. Visser, *J. Appl. Crystallogr.* **2,** 89 (1969).
8. K. Yvon, W. Jeitschko, and E. Parthé, *J. Appl. Crystallogr.* **10,** 73 (1977).
9. G. M. Sheldrick, SHELXS-86, University of Cambridge, Cambridge, England, 1986.
10. G. M. Sheldrick, "SHELXL-93, A Program for Crystal Structure Determination," University of Göttingen, Göttingen, 1993.
11. J. Rodriguez-Carvajal, "FULLPROF Version 2.6.1. Oct. 94, ILL." [Unpublished; based on the original code provided by D. B. Wiles and A. Sakthivel, *J. Appl. Crystallogr.* **14,** 149 (1981)]
12. F. H. Spedding, K. A. Gschneidner, Jr., and A. H. Daane, *J. Am. Chem. Soc.* **80,** 4499 (1958).
13. R. Pöttgen and W. Jeitschko, *Z. Naturforsch. B* **47,** 358 (1992).
14. R. Hoffmann and H.-J. Meyer, *Z. Anorg. Allg. Chem.* **607,** 57 (1992).
15. F. H. Pollard, G. Nickless, and S. Evered, *J. Chromatogr.* **15,** 211 (1964).
16. W. Jeitschko, M. H. Gerss, R.-D. Hoffmann, and St. Lee, *J. Less-Common Met.* **156,** 397 (1989).
17. J. F. Cordes and K. Wintersberger, *Z. Naturforsch. B* **12,** 136 (1957).
18. H. Fjellvåg and P. Karen, *Inorg. Chem.* **31,** 3260 (1992).