Preparation and crystal structure of the carbides $R_{11}Ni_{60}C_6$ ($R \equiv Y$, Dy–Lu)

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Abstract

The carbides $R_{11}Ni_{60}C_6$ ($R \equiv Y$, Dy–Lu) were prepared from powders of the elemental components by arc-melting of cold-pressed pellets and subsequent annealing. They crystallize with a cubic structure of space group $Im\bar{3}m$ which was determined from single-crystal X-ray data of $Yb_{11}Ni_{60}C_6$ ($a = 1244.1(1)$ pm, $Z = 2$) and refined to a residual of $R = 0.024$ for 257 structure factors and 26 variable parameters. The metal atoms have high coordination numbers, as is typical of intermetallic phases. The carbon atoms occupy an octahedral site with one ytterbium and five nickel atoms as neighbours. This is only partially reflected by the hydrolysis of $Lu_{11}Ni_{60}C_6$ in diluted hydrochloric acid which results in mainly methane with substantial amounts of ethane and ethylene. The compounds are ferromagnetic.

1. Introduction

During the last few years, several ternary lanthanoid transition-metal carbides have been found with a rather high transition metal content while the carbon content is low. With manganese as the transition metal, three structure types were reported: $Pr_2Mn_{17}C_{3-x}$ [1], $Tb_2Mn_{17}C_{3-x}$ [2] and $LaMn_{11}C_{2-x}$ [3]. The iron-containing carbides $Ln_2Fe_{14}C$ (where Ln is a lanthanoid) [4–13] and $Ln_2Fe_{17}C_{3-x}$ [14, 15] were explored extensively because of their interesting magnetic properties. Stadelmaier and Liu [16] reported a cobalt-containing phase "$Sm_5Co_{11}C_2$" with as yet unknown crystal structure. Finally, with nickel as the transition metal, the carbides $Ln_2Ni_{22}C_3$ have been known for some time [17].

In the present paper we report on another series of carbides with high nickel content, one member of these was identified some time ago with the approximate composition "$Y_5Ni_{29}C_3$" [18]. After completion of our manuscript, we found that the crystal structure of these isotypic compounds had already been determined for two members of this series: for the yttrium compound from powder data [19, 20] and for the thulium compound from single-crystal data [21]. Our determination of the structure of the ytterbium compound is considerably more accurate than the previous investigations. The compounds $Dy_{11}Ni_{60}C_6$ and $Ho_{11}Ni_{60}C_6$ are reported here for the first time.

2. Sample preparation and characterization

The ternary carbides were prepared from the elemental components by arc-melting with subsequent annealing at 750 °C for 10 days. The filings of the rare earth metals and the nickel powder had nominal purities of 99.9%. They were mixed in the ideal ratio with graphite ("specpure"), pressed to pellets and arc-melted under purified argon. While the erbium, thulium, ytterbium and lutetium compounds were present already in the "as cast" alloys, the yttrium, dysprosium and holmium compounds were formed only after the annealing.

The reaction products were characterized through their Guinier powder patterns. The lattice constants (Table 1) were refined by least-squares fits using α-quartz ($a = 491.30$ pm, $c = 540.46$ pm) as a standard. As an example the evaluation of the powder pattern of $Dy_{11}Ni_{60}C_6$ is shown in Table 2. Stadelmaier and Kim [18] reported a powder pattern for "$Y_5Ni_{29}C_3$". Our evaluation of this pattern resulted in the lattice constant of $a = 1249.5(3)$ pm which agrees well with the results from our sample.

The compact samples have metallic lustre and are not sensitive to air. The powders are black. They hydrolyse in 2 N hydrochloric acid. The gaseous reaction products of a sample of $Lu_{11}Ni_{60}C_6$ were analysed in a gas chromatograph. They consisted mainly of hydrogen as carrier gas with (in weight per cent) $78CH_4$, $8C_2H_6$ and $14C_2H_4$. It has been shown before that the hydrolysis products of complex carbides do not necessarily correspond to the bonding of the carbon atoms in the solid [23]. Nevertheless, since the structure determination shows that there are no carbon pairs in the compound it is not surprising that the main product is methane.

All of these ternary carbides are strongly attracted by a magnet at room temperature. A detailed investigation of the ferromagnetic properties of these compounds is in progress.

TABLE 1

Lattice constants of the cubic compounds $R_{11}Ni_{60}C_6$

Compound	a (pm)	V (nm^3)
$Y_{11}Ni_{60}C_6$	1251.1(1)	1.9584(3)
$Dy_{11}Ni_{60}C_6$	1249.5(1)	1.9509(3)
$Ho_{11}Ni_{60}C_6$	1248.0(1)	1.9438(3)
$Er_{11}Ni_{60}C_6$	1245.9(1)	1.9342(3)
$Tm_{11}Ni_{60}C_6$	1242.7(1)	1.9192(3)
$Yb_{11}Ni_{60}C_6$	1244.1(1)	1.9256(3)
$Lu_{11}Ni_{60}C_6$	1241.4(1)	1.9131(3)

Standard deviations in the positions of the last digits are given in parentheses throughout the paper.

TABLE 2

Guinier powder pattern of $Dy_{11}Ni_{60}C_6$[a]

hkl	Q_c	Q_o	I_c	I_o	hkl	Q_c	Q_o	I_c	I_o
110	128	–	<1	–	444	3074	–	1	–
200	256	258	2	vw	710			6	
211	384	384	2	vw	543	3202	3201	3	m
220	512	513	4	w	550			2	
310	640	641	5	w	640	3330	3332	1	vw
222	769	768	1	vw	633			1	
321	897	894	2	vw	552	3459	3459	2	w
400	1024	1026	1	vw	721			2	
330	1153	1153	14	s	642	3587	3589	3	vw
410			4		730	3715	3715	3	vw
420	1281	1281	25	s	732	3971	3972	4	w
332	1409	1409	29	s	651			<0	
422	1537	1538	4	w	800	4099	–	<0	–
431	1665	1667	<1	vw	811			2	
510			<1		741	4227	4210	3	m
521	1921	1916	3	w	554			3	
440	2050	2049	9	m	644	4355	4359	2	m
530	2178	2178	61	vs	820			5	
433			100		653	4483	4482	10	m
442	2306	2305	3	vs	822	4611	4611	1	s
600			74		660			22	
611	2435	2433	<1	m	831			<1	
532			12		743	4800	–	<1	–
620	2562	–	<1	–	750			1	
541	2690	2688	6	w	662	4867	–	<1	–
622	2818	2821	1	vw	752	4996	4995	4	w
631	2946	2944	4	w	840	5122	5122	12	m

[a]The intensities were calculated [22] with the positional parameters obtained for $Yb_{11}Ni_{60}C_6$. Cu $K\alpha$ radiation, $Q = 100/d^2$ (nm^{-2}). The observed intensities I_o from very weak to very strong are abbreviated: vw, w, m, s, vs.

3. Crystal structure of $Yb_{11}Ni_{60}C_6$

The single crystal (dimensions $20 \times 15 \times 40$ μm^3) used for the structure determination was isolated from a crushed sample with the atomic ratio Yb:Ni:C = 3:15:2. The sample had been arc-melted and subsequently annealed in a high-frequency furnace for 30 min just below the melting temperature.

The crystal was investigated in a precession camera. It showed a b.c.c. cell with high Laue symmetry. There are $Z = 2$ formula units per cell. Intensity data were measured in a four-circle diffractometer with graphite-mono-chromated Mo $K\alpha$ radiation, a scintillation counter and a pulse-height dis-criminator. We recorded $\theta/2\theta$ scans with background counts on both sides of each scan up to $2\theta = 70°$ in one eighth of the reciprocal cell. An absorption correction was applied from psi-scan data. The ratio of the highest to the

lowest transmission was 1.38. A total of 4505 reflections was measured; 453 resulted after data averaging and 257 remained after omitting those with intensities $I < 1\sigma(I)$.

The structure was determined and refined in space group $Im\bar{3}m$ (number 229). The positions of the ytterbium atoms were obtained by an evaluation of a Patterson synthesis, the other atoms were located through difference Fourier syntheses. For the least-squares refinements, atomic scattering factors [24] were used, corrected for anomalous dispersion [25]. A parameter accounting for isotropic secondary extinction was refined and the weights were according the counting statistics. In one series of least-squares cycles,

TABLE 3

Atomic parameters of $Yb_{11}Ni_{60}C_6$[a]

Atom	$Im\bar{3}m$	Occupancy (%)	x	y	z	B_{eq}
Yb1	16f	99.5(2)	0.16817(3)	x	x	0.503(2)
Yb2	6b	101.2(4)	0	1/2	1/2	0.59(1)
Ni1	48k	100.3(3)	0.32644(6)	x	0.09298(8)	0.49(1)
Ni2	48j	100.2(3)	0	0.14866(9)	0.31742(9)	0.55(2)
Ni3	12e	101.8(7)	0.1446(2)	0	0	0.73(3)
Ni4	12d	100.8(7)	1/4	0	1/2	0.54(3)
C1	12e	93(5)	0.2944(15)	0	0	0.6(2)

[a]The program STRUCTURE TIDY [26] was used to standardize the positional parameters. The occupancy parameters were obtained in a separate series of least-squares cycles. The last column contains the isotropic thermal parameter of the carbon atoms and the equivalent isotropic thermal parameter B_{eq} ($\times 100$, in units of nm^2) of the anisotropic parameters of the metal atoms.

TABLE 4

Interatomic distances in $Yb_{11}Ni_{60}C_6$[a]

Yb1:	6 Ni2	280.8(1)	Ni1:	1 Ni1	231.4(1)	Ni2:	1 Cl	187.2(3)
	3 Ni1	293.8(1)		2 Ni1	237.2(1)		2 Ni1	245.0(1)
	3 Ni1	297.3(1)		2 Ni2	245.0(1)		2 Ni1	249.9(1)
	3 Ni3	297.3(1)		2 Ni2	249.9(1)		1 Ni4	259.8(1)
	1 Yb1	352.7(1)		2 Ni4	262.8(1)		2 Ni2	261.6(1)
				1 Yb1	293.8(1)		2 Yb1	280.8(1)
Yb2:	2 Cl	256(2)		1 Yb1	297.3(1)		1 Ni3	283.6(2)
	8 Ni2	292.9(1)		1 Yb2	326.5(1)		1 Yb2	292.9(1)
	4 Ni4	311.0(1)					1 Ni2	296.9(2)
	8 Ni1	326.5(1)	Ni3:	1 Cl	186(2)			
				4 Ni3	254.4(3)	Ni4:	4 Ni2	259.8(1)
C1:	1 Ni3	186(2)		4 Ni2	283.6(2)		8 Ni1	262.8(1)
	4 Ni2	187.2(3)		4 Yb1	297.3(1)		2 Yb1	311.0(1)
	1 Yb2	256(2)						

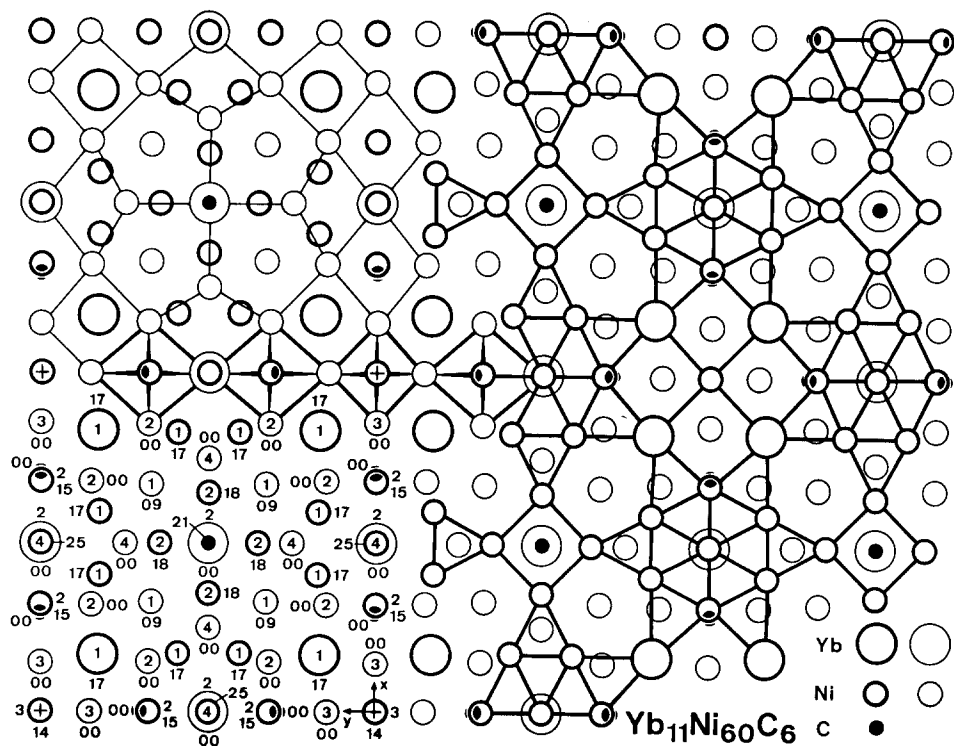[a]All distances shorter than 410 pm (Yb–Yb, Yb–Ni) and 330 pm (Ni–Ni, Yb–C, Ni–C, C–C) are listed.

Fig. 1. The structure of $Yb_{11}Ni_{60}C_6$. Only one half of the c.b.c. cell from $z = -1/4$ to $z = 1/4$ is shown. There is a mirror plane at $z = 0$ and only the heights of the atoms with positive z values are given in hundredths in the lower left-hand corner of the drawing. One-digit numbers correspond to the atom designations. In the right-hand part of the drawing atoms at $z = 0.14$ to $z = 0.18$ are connected by thick lines; in the upper left-hand corner thin lines connect atoms at $z = 0$. Directly below this part of the drawing we have outlined a horizontal string of corner sharing carbon filled $YbNi_5$ octahedra and empty Ni_6 octahedra.
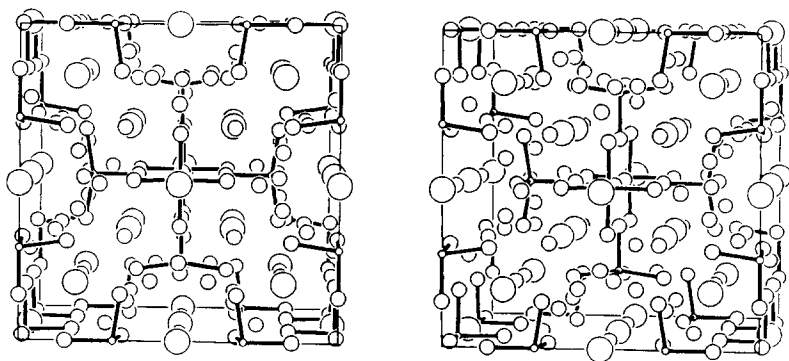
Fig. 2. Stereoplot of one unit cell of the cubic $Yb_{11}Ni_{60}C_6$ structure. Large atoms are ytterbium, medium sized atoms are nickel. Nickel–carbon bonds are outlined.
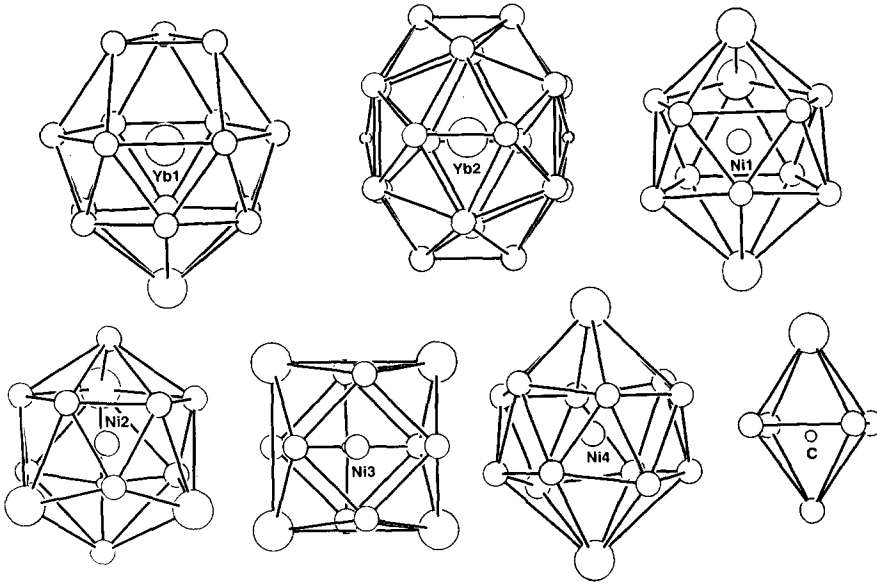
Fig. 3. Coordination polyhedra in $Yb_{11}Ni_{60}C_6$. All polyhedra have mirror planes approximately perpendicular to the projection direction.
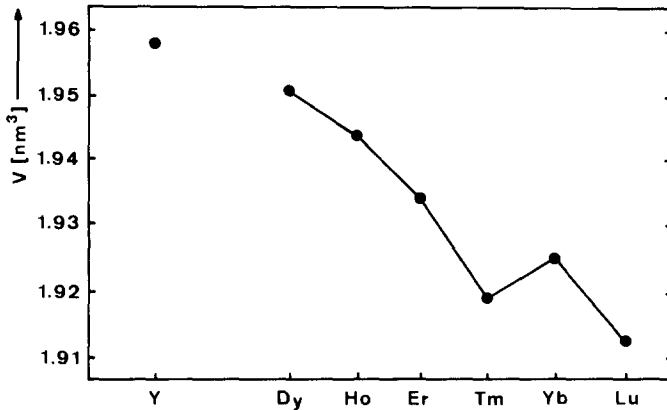

Fig. 4. Average atomic volumes of the $R_{11}Ni_{60}C_6$ carbides.

occupancy parameters were refined. No significant deviations from the ideal composition were observed. In the final cycles the ideal occupancies were assumed. A final difference Fourier analysis showed no electron densities at sites suitable for additional atomic positions. The highest peak of 1.9 electrons/ $Å^3$ was only 23 pm from the Ni1 position. The final residual is $R = 0.024$ for 26 variable parameters and 257 structure factors. The atomic parameters and interatomic distances are given in Tables 3 and 4. A listing of the anisotropic thermal parameters and structure factors can be obtained from the authors [27]. Part of the structure is projected in Fig. 1, a stereoprojection is shown in Fig. 2.

4. Discussion

In the structure of $Yb_{11}Ni_{60}C_6$ all the metal atoms have high coordination numbers (CN) (Fig. 3), as is typical of intermetallic compounds. The ytterbium atoms occupy two different sites with quite different environments. The Yb1 atoms have CN 16 (15Ni + 1Yb) while the Yb2 atoms have CN 22 (20Ni + 2C). The average Yb–Ni distances of 290.0 pm and 310.0 pm respectively, reflect this different coordination. The plot of the average atomic volumes of the $R_{11}Ni_{60}C_6$ series (Fig. 4) suggests that the ytterbium atoms have a partial divalent character. It is likely that the ytterbium atoms of the two different sites have different valences in $Yb_{11}Ni_{60}C_6$ with divalent and trivalent ytterbium atoms preferring the Yb2 and Yb1 sites respectively.

The Ni1 and Ni2 atoms have 12 metal neighbours forming distorted icosahedra. In addition, each Ni2 atom has one carbon neighbour. The Ni3 atoms also have 12 metal neighbours: eight nickel atoms forming a distorted cube and four ytterbium atoms capping four of the six cube faces. The fifth of the cube faces contains a carbon atom, while the sixth remains uncapped. The Ni4 atom has CN 14 and corresponds to the Frank–Kasper polyhedron [28] with that CN. It has 12 nickel atoms at the 12 corners where five triangular faces meet and two ytterbium atoms at the two corners common to six triangular faces.

The carbon atoms occupy octahedral voids formed by five nickel and one ytterbium atom. It is noteworthy that not all octahedral voids are filled in $Yb_{11}Ni_{60}C_6$. The octahedral void at the origin of the cell has six Ni3 neighbours at a distance of 179.9 pm. This distance is only slightly shorter than the average Ni–C distance of 187.0 pm in the compound. A carbon filled octahedral void formed exclusively by nickel atoms is found in the structure of $Th_3Ni_5C_5$. There the average Ni–C distance is 184.5 pm [29].

The structures of $Pr_2Mn_{17}C_{3-x}$ [1], $Tb_2Mn_{17}C_{3-x}$ [2] and $LaMn_{11}C_{2-x}$ [3] may be regarded as "filled up" versions of the binary structure types Th_2Zn_{17}, Th_2Ni_{17} and $BaCd_{11}$ respectively, where the carbon atoms occupy octahedral voids of the binary structure [30]. For the structure of $Yb_{11}Ni_{60}C_6$ no such binary type has yet been found [20]. This is also the case for $Ce_2Ni_{22}C_3$ [17]. The latter compound is also remarkable because there some carbon atoms are reported to have only five nickel neighbours.

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