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Structure refinement of $Ce_2Ni_{22}C_{3-x}$ and properties of the isotypic carbides $Ln_2Ni_{22}C_{3-x}$ (Ln≡La–Nd, Sm, Gd–Ho)

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Abstract

The crystal structure of $Ce_2Ni_{22}C_{3-x}$ (*Cmca*, $a = 1137.3(2)$ pm, $b = 1500.4(3)$ pm, $c = 1462.5(4)$ pm, $V = 2.4956$ nm^3, $Z = 8$) is confirmed. It was refined from single-crystal X-ray data to a residual $R = 0.021$ (1464 structure factors and 130 variable parameters). The positions of the carbon atoms in the trigonal prisms of nickel atoms are fully occupied, while the other positions within the trigonal bipyramids were found to be occupied only to 75(3)%. This corresponds to the composition $Ce_2Ni_{22}C_{2.75}$. The specific conductivities of most compounds exhibit metallic behaviour with an increase in the resistance by a factor of about 2 between 2 K and 300 K. In contrast, the cerium compound exhibits almost temperature-independent conductivity, which is possibly due to an intermediate valence of the cerium atoms. This can also be inferred from the plot of the cell volumes of these compounds. All compounds are ferromagnetic at room temperature.

1. Introduction

Bodak *et al.* investigated the three carbides $Ln_2Ni_{22}C_3$ (Ln≡La, Ce, Pr). Their crystal structure was determined for the cerium compound from single-crystal data and refined to a residual $R = 0.082$ [1]. Subsequently Putyatin and coworkers [2–4] prepared at high pressure the whole series of isotypic carbides with Ln≡La–Nd, Sm, Gd–Lu. They ascribed them to the composition $LnNi_8C_2$ on the basis of metallographic investigations of the La–Ni–C ternary system. They correctly assumed that these compounds are isotypic with $Ce_2Ni_{22}C_3$; however, since some of the interatomic distances appeared to be rather short, they had doubts about the crystal structure and recommended a reinvestigation. We were interested in the structure of these carbides in the course of our investigations on carbides of similar composition, *e.g.* $Pr_2Mn_{17}C_{3-x}$ [5], $Tb_2Mn_{17}C_{3-x}$ [6], $LaMn_{11}C_{2-x}$ [7] and $Yb_{11}Ni_{60}C_6$ [8]. The crystal structure of $Ce_2Ni_{22}C_3$ is essentially confirmed. In addition we report some physical properties of these compounds.

2. Sample preparation and lattice constants

The compounds were prepared from the elemental components (metals with nominal purities greater than 99.9%, graphite flakes of purity 99.5%)

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by arc melting cold-pressed pellets of the ideal composition in an atmosphere of argon (99.996%). The argon was purified by repeatedly melting a titanium button before the reactions. For the annealing processes (10 days at 850 °C) the samples were wrapped in tantalum foil and enclosed in evacuated silica tubes.

Using these preparation conditions, we obtained the compounds with La–Nd, samarium and Gd–Ho. Putyatin and Sevast'yanova [4] additionally reported the four compounds $LnNi_8C_2$ (Ln≡Er–Lu) which were obtained by annealing at high temperatures and high pressures. We have not (yet) obtained these compounds, neither in the arc-melted samples nor in the samples annealed at 850 °C, 1000 °C or 1200 °C. The Guinier powder diagrams of these samples always revealed the carbides with the $Yb_{11}Ni_{60}C_6$ type of structure [8].

Energy–dispersive X-ray fluorescence analyses in a scanning electron microscope did not reveal any contamination by elements heavier than sodium. The Guinier powder patterns of the samples indicated single-phase products. The lattice constants (Table 1) were obtained by least-squares fits of the Guinier data using Cu $K\alpha_1$ radiation and α-quartz ($a = 491.30$ pm, $c = 540.46$ pm) as a standard. The identification of the diffraction lines was facilitated by intensity calculations [9] using the positional parameters of the refined structure. In the case of $Ce_2Ni_{22}C_{3-x}$ the lattice constants determined on the four-circle diffractometer were in good agreement with those obtained from the powder data. The plot of the cell volumes (Fig. 1) shows the expected lanthanoid contraction. The deviation for the cerium compound indicates the (at least partial) tetravalent character of this element.

TABLE 1

Lattice constants of the orthorhombic $Ce_2Ni_{22}C_{3-x}$-type carbides[a]

Compound	a (pm)	b (pm)	c (pm)	V (nm^3)	Reference
$La_2Ni_{22}C_3$	1142.5(5)	1513.7(3)	1474.3(3)	2.5497	This work
$La_2Ni_{22}C_3$	1145(5)	1512(4)	1463(4)	2.5328	[1]
$Ce_2Ni_{22}C_{2.75}$	1137.3(2)	1500.4(3)	1462.5(4)	2.4956	This work
$Ce_2Ni_{22}C_3$	1138.4(3)	1502.4(7)	1467.1(5)	2.5092	[1]
$Pr_2Ni_{22}C_3$	1139.6(3)	1505.9(4)	1468.4(3)	2.5201	This work
$Pr_2Ni_{22}C_3$	1138(4)	1505(3)	1459(3)	2.4988	[1]
$Nd_2Ni_{22}C_3$	1138.6(2)	1506.6(3)	1466.5(3)	2.5155	This work
$Sm_2Ni_{22}C_3$	1136.4(3)	1501.3(4)	1460.5(6)	2.4916	This work
$Gd_2Ni_{22}C_3$	1136.1(2)	1498.0(3)	1457.0(2)	2.4796	This work
$Tb_2Ni_{22}C_3$	1134.4(2)	1497.3(3)	1457.4(4)	2.4754	This work
$Dy_2Ni_{22}C_3$	1133.4(4)	1495.7(3)	1453.9(6)	2.4649	This work
$Ho_2Ni_{22}C_3$	1134.2(4)	1494.8(5)	1452.9(6)	2.4631	This work

[a] Here and in the following tables standard deviations in the positions of the least significant digits are given in parentheses.

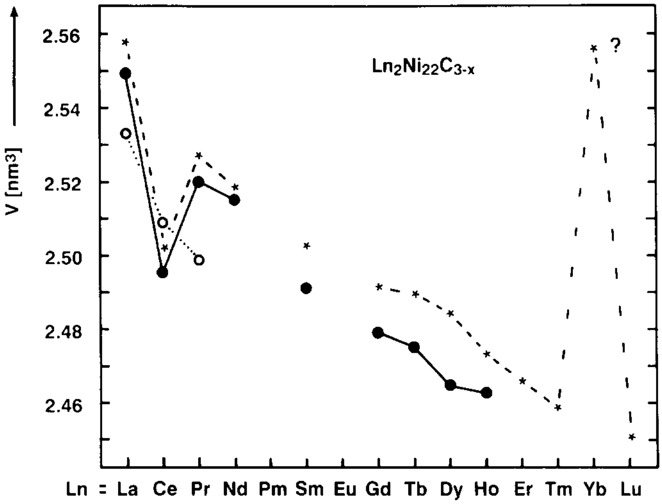

Fig. 1. Cell volumes of the orthorhombic carbides with $Ce_2Ni_{22}C_{3-x}$-type structure. ●, obtained in the present investigation; ○, reported by Bodak *et al.* [1]; *, volumes of carbides originally reported with the tentative composition $LnNi_8C_2$ [2–4] which presumably are isotypic with $Ce_2Ni_{22}C_{3-x}$.

3. Properties

The samples with La–Nd as the rare earth components were very well crystallized, while the others were more or less microcrystalline. Single crystals of the $Ln_2Ni_{22}C_{3-x}$ compounds are grey with some metallic lustre. The powdered samples of the compounds are dark grey and stable in air for long periods of time. The samples do not visibly hydrolyse in water. They slowly dissolve in diluted hydrochloric acid.

The electrical conductivity behaviour of several samples was determined from single crystals for the lanthanum, cerium, praseodymium and neodymium compounds and from polycrystalline samples for the samarium and Gd–Dy compounds with an a.c. four-probe device in the temperature range from 2 to 300 K. The single crystals and the polycrystalline samples all had a size of about 0.5 × 0.5 × 0.5 mm. Four copper filaments were glued to the samples with a silver–epoxy cement. At two contacts a constant alternating current was maintained through the whole sample and the voltage difference was measured at the other two contacts. The absolute values are estimated to be correct only within a factor of 2 because of the irregular shapes of the samples and the problems in measuring the distances between the relatively large contact areas. The relative values for one sample at different temperatures, however, are much more reliable.

The specific electrical resistivities of all compounds decrease with temperature (Fig. 2) as is typical for metallic conductors. This behaviour was expected because of the high metal content of these carbides. The absolute values of the resistivities range from 80 $\mu\Omega$ cm to 700 $\mu\Omega$ cm. Considering

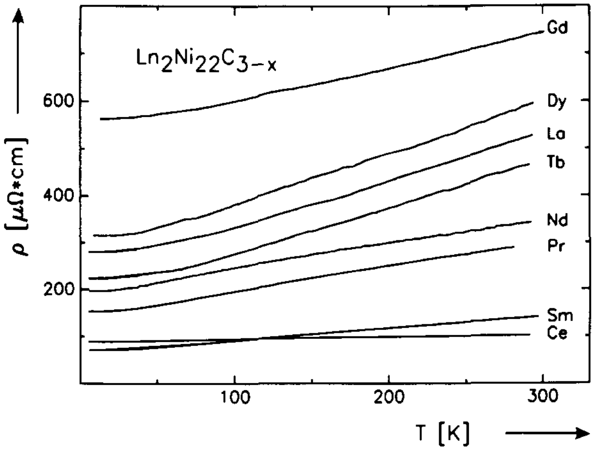

Fig. 2. Specific resistivities of the carbides $Ln_2Ni_{22}C_{3-x}$ (Ln≡La–Nd, Sm, Gd–Dy). The relative resistivities of one sample as a function of temperature are reliable. The absolute values from one sample to another are estimated to be correct only within a factor of 2.

that these values are only correct within a factor of 2, one may assume that the electrical conductivity behaviours of all compounds are essentially equal. The resistivities are rather high, when compared with the values $\rho = 1.59$ μΩ cm and $\rho = 6.84$ μΩ cm for the very good metallic conductors silver and nickel. Our values are of about the same magnitude as the values of 88 μΩ cm and 140 μΩ cm for the lanthanoids samarium and gadolinium [10]. The temperature dependence of the resistivity of the cerium compound is considerably smaller than that of the other compounds. This behaviour is possibly due to the intermediate valent character of the cerium atoms as already mentioned with regard to the cell volumes.

All of our samples are strongly attracted by a magnet at room temperature. A more detailed characterization of the ferromagnetic properties of these carbides is in progress.

4. Structure refinement

A well-crystallized sample of $Ce_2Ni_{22}C_3$ was obtained by annealing an arc-melted button of the nominal composition in an evacuated silica tube slightly below the melting point for about 10 h in a high frequency furnace. The single crystals isolated from the crushed sample were investigated with a Buerger precession camera to establish their symmetry and their suitability for intensity data collection. The crystal selected had the form of a prism with the dimensions of 20×20×110 μm. 11357 reflections were recorded in one-half of the reciprocal sphere up to $2\theta = 70°$ in an automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation, a scintillation counter and a pulse–height discriminator. The background was determined at both ends of each θ–2θ scan. An empirical absorption correction was made from psi scan data. After averaging the equivalent reflections and omitting those with $F_0 < 3\sigma(F_0)$, 1464 structure factors remained which were used for the structure refinement.

The positions of the lanthanoid and nickel atoms were assumed to be correctly determined in the previous structure determination of $Ce_2Ni_{22}C_3$ [1]. Those of the carbon atoms were obtained from difference Fourier syntheses. The structure was refined in the highest symmetry space group compatible with the space group extinctions, *Cmca*, with a full-matrix least-squares program using atomic scattering factors [11], corrected for anomalous dispersion [12]. The weighting scheme was based on the counting statistics. A parameter for an isotropic secondary extinction correction was refined and applied to the calculated structure factors. In a separate least-squares cycle the scale factor was held constant and all occupancy parameters were allowed to vary. The metal atoms exhibited no significant deviations from the full occupancies. For the C2 position the occupancy was 106(2)%; the C1 position was only occupied to 75(3)% with a thermal parameter $B = 1.5(2) \times 100$ nm^2. When the thermal parameter of the C1 atom was held at the value of the C2 atom ($B = 0.5 \times 100$ nm^2), an occupancy of 66(2)% was obtained. Thus, the C1 position exhibits a significant deviation from the full occupancy. This was also observed for the manganese-rich carbides $Pr_2Mn_{17}C_{3-x}$ [5], $Tb_2Mn_{17}C_{3-x}$ [6] and $LaMn_{11}C_{2-x}$ [7].

In the final least-squares cycles the ideal occupancies were assumed with the exception of that for the C1 position. The metal atoms were refined with anisotropic and the carbon atoms with isotropic thermal parameters. The final unweighted and weighted residuals are $R = 0.021$ and $R_w = 0.021$ respectively (1464 structure factors and 130 variable parameters). A final difference Fourier synthesis revealed as the highest peak an electron density of 2.1×10^3 e.nm^{-3}. This peak was too close to the position of one nickel atom to be suitable for an additional atomic site. The atomic parameters and interatomic distances are listed in Tables 2 and 3. Stereoplots of the structure are shown in Fig. 3. Tables with the anisotropic thermal parameters of the metal atoms and the observed and calculated structure factors are available from the authors.

5. Discussion

The present structure refinement of $Ce_2Ni_{22}C_3$ is considerably more accurate than the previous refinement [1]. The occupancy parameters of the metal atoms vary between 0.986(3) for Ni2 and 1.006(1) for Ce1, and thus the structure refinement gives no indication of a deviation from the ideal Ce:Ni ratio. The thermal parameters of the metal atoms are all slightly higher than expected, indicating that the scan widths at high θ angles were slightly too short. The greatest difference in the positions of the metal atoms between the earlier and the present structure determination is in the z parameter of the Ni11 atom which is 0.1733(6) in the earlier work as compared with

TABLE 2

Atomic parameters of $Ce_2Ni_{22}C_{2.75}$[a]

Atom	*Cmca*	Occupancy	*x*	*y*	*z*	*B* (×100 nm^2)
Ce1	8e	1.006(1)	0.25	0.06520(3)	0.25	0.555(7)
Ce2	8f	1.002(1)	0	0.20722(3)	0.97170(4)	0.613(7)
Ni1	16g	0.996(2)	0.17933(7)	0.25034(6)	0.31785(5)	0.53(1)
Ni2	8f	0.986(3)	0	0.06160(8)	0.15674(8)	0.62(2)
Ni3	16g	0.998(2)	0.38943(7)	0.11915(5)	0.07795(5)	0.54(1)
Ni4	16g	1.000(2)	0.17469(7)	0.07617(5)	0.04909(5)	0.54(1)
Ni5	16g	0.990(2)	0.17640(7)	0.46388(5)	0.07321(5)	0.47(1)
Ni6	16g	0.995(2)	0.10782(7)	0.21317(5)	0.15618(5)	0.51(1)
Ni7	16g	1.000(2)	0.37497(8)	0.07595(5)	0.63123(6)	0.85(1)
Ni8	16g	0.990(2)	0.16922(7)	0.37609(5)	0.20191(6)	0.62(1)
Ni9	8f	0.995(3)	0	0.31930(8)	0.26656(8)	0.59(2)
Ni10	8f	1.003(3)	0	0.35527(8)	0.08601(8)	0.58(2)
Ni11	8f	1.001(4)	0	0.49703(9)	0.1771(1)	1.16(2)
Ni12	8f	0.988(3)	0	0.15844(8)	0.28814(8)	0.55(2)
Ni13	4b	0.990(5)	0.5	0	0	0.52(3)
Ni14	16g	1.004(2)	0.27853(7)	0.31143(5)	0.45142(5)	0.51(1)
Ni15	4a	0.993(5)	0	0	0	0.62(3)
C1	8f	0.75(3)	0	0.4459(6)	0.2854(6)	1.5(2)
C2	16g	1.06(2)	0.2440(6)	0.1871(4)	0.0848(4)	0.50(7)

[a] The last column contains the isotropic *B* values of the carbon positions and the equivalent isotropic *B* values of the ellipsoidal thermal parameters of the metal positions. The occupancy parameters were obtained in a separate least-squares cycle in a refinement together with variable thermal parameters. In the final runs the ideal occupancies were assumed with the exception of the occupancy parameter of the C2 position.

0.1771(2) here. Thus, with the exception of the partial occupancy of the C1 position the original structure determination is essentially confirmed.

Putyatin *et al.* [2] had doubts about the correctness of the previous structure determination not only because their metallographic examinations resulted in the composition $LaNi_8C_2$ (9.1:72.7:18.2 as compared with 7.5:82.2:10.3 for $Ce_2Ni_{22}C_{2.75}$), but also because some interatomic distances seemed to be rather short. The shortest Ce–Ni distance was 276(1) pm in the earlier investigation. It is 278.1(1) pm in the present work. Admittedly this is a rather short distance, considering the sum of the coordination number 12 radii of 305 pm; however, in the structures of Ce_7Ni_3 [13], $CeNi_3$ [14] and Ce_2Ni_7 [15] the shortest Ce–Ni distances of 283(3) pm, 286(1) pm and 283(1) pm are only slightly greater. The shortest Ni–Ni distance in the previous investigation was 231(1) pm. In the present investigation it is even shorter: 229.9(1) pm. A similar short Ni–Ni distance of 231.4(1) pm was found in $Yb_{11}Ni_{60}C_6$ [8]. Finally, the shortest Ni–C distance of the previous structure determination was 180(8) pm as compared with 176(1) pm found here. This short Ni–C distance is certainly related to the unusual nickel environment of the C1 atoms in the structure. This is the only rare earth–transition metal carbide with trigonal bipyramidal carbon coordination

TABLE 3

Interatomic distances (pm) in the structure of $Ce_2Ni_{22}C_{2.75}$

Ce1	2	Ni1	305.7(1)	Ni5	1	Ni8	229.9(1)	Ni11	1	C1	176(1)
	2	Ni8	306.4(1)		1	Ni13	233.8(1)		1	Ni12	247.5(2)
	2	Ni4	306.5(1)		1	Ni14	237.2(1)		1	Ni10	251.0(2)
	2	Ni6	307.0(1)		1	Ni5	240.0(1)		2	Ni5	256.6(1)
	2	Ni3	308.2(1)		1	Ni4	241.5(1)		1	Ni13	259.1(2)
	2	Ni7	308.6(1)		1	Ni3	244.8(1)		1	Ni2	261.6(2)
	2	Ni5	311.4(1)		1	Ni7	248.5(1)		2	Ni3	265.4(1)
	2	Ni2	315.4(1)		1	Ni4	253.5(1)		2	Ni8	267.0(1)
	2	Ni11	320.4(1)		1	Ni11	256.6(1)		1	Ni9	297.0(2)
	2	Ni12	321.8(1)		1	Ni10	259.1(1)		2	Ce1	320.4(1)
Ce2	2	Ni10	278.0(1)		1	Ni3	264.6(1)	Ni12	2	Ni3	240.1(1)
	2	Ni7	285.8(1)		1	Ce1	311.4(1)		1	Ni2	240.9(2)
	2	Ni6	296.5(1)	Ni6	1	C2	190.8(7)		2	Ni6	243.0(1)
	2	Ni3	298.3(1)		1	Ni12	243.0(1)		1	Ni9	243.4(2)
	2	Ni4	301.6(1)		1	Ni6	245.3(1)		1	Ni11	247.5(2)
	1	Ni9	302.6(1)		1	Ni1	251.3(1)		2	Ni1	250.0(1)
	2	Ni1	310.3(1)		1	Ni14	251.4(1)		2	Ce1	321.8(1)
	1	Ni15	313.7(1)		1	Ni1	256.2(1)		1	Ce2	335.7(1)
	2	Ni14	317.1(1)		1	Ni9	257.8(1)	Ni13	4	Ni5	233.8(1)
	2	Ni14	319.4(1)		1	Ni2	258.4(1)		4	Ni3	246.5(1)
	1	Ni12	335.7(1)		1	Ni8	262.9(1)		2	Ni10	251.0(1)
	1	Ni2	347.8(1)		1	Ni10	266.5(1)		2	Ni11	259.1(2)
Ni1	1	C2	192.0(6)		1	Ni4	269.4(1)	Ni14	1	C2	195.6(6)
	1	Ni9	240.7(1)		1	Ce2	296.5(1)		1	C2	199.0(6)
	1	Ni14	243.5(1)		1	Ce1	307.0(1)		1	Ni5	237.2(1)
	1	Ni12	250.0(1)	Ni7	1	C1	190.1(7)		1	Ni14	241.6(1)
	1	Ni6	251.3(1)		1	Ni5	248.5(1)		1	Ni1	243.5(1)
	1	Ni8	253.9(1)		1	Ni2	253.4(1)		1	Ni3	247.0(1)
	1	Ni1	255.4(1)		1	Ni8	259.3(1)		1	Ni4	250.6(1)
	1	Ni6	256.2(1)		1	Ni9	259.4(1)		1	Ni6	251.4(1)
	1	Ni8	257.1(1)		1	Ni4	264.0(1)		1	Ni8	251.5(1)
	1	Ni3	260.9(1)		1	Ni15	264.7(1)		1	Ni10	266.0(1)
	1	Ni7	278.0(1)		1	Ni8	265.7(1)		1	Ni7	271.4(1)
	1	Ce1	305.7(1)		1	Ni4	269.7(1)		1	Ce2	317.1(1)
	1	Ce2	310.3(1)		1	Ni14	271.4(1)		1	Ce2	319.4(1)
Ni2	1	C1	193(1)		1	Ni1	278.0(1)	Ni15	4	Ni4	240.2(1)
	1	Ni12	240.9(2)		1	Ni7	284.4(1)		2	Ni2	247.2(1)
	1	Ni15	247.2(1)		1	Ce2	285.8(1)		4	Ni7	264.7(1)
	2	Ni7	253.4(1)		1	Ce1	308.6(1)		2	Ce2	313.7(1)
	2	Ni4	254.4(1)	Ni8	1	Ni5	229.9(1)	C1	1	Ni11	176(1)
	2	Ni6	258.4(1)		1	Ni9	230.7(1)		2	Ni7	190.1(7)
	1	Ni11	261.6(2)		1	Ni8	231.4(1)		1	Ni9	191.9(9)
	2	Ce1	315.4(1)		1	Ni14	251.5(1)		1	Ni2	193(1)
	1	Ce2	347.8(1)		1	Ni1	253.9(1)	C2	1	Ni6	190.8(7)
Ni3	1	C2	194.6(7)		1	Ni1	257.1(1)		1	Ni4	191.5(6)
	1	Ni12	240.1(1)		1	Ni10	258.4(1)		1	Ni1	192.0(6)
					1	Ni7	259.3(1)				
					1	Ni6	262.9(1)				
					1	Ni7	265.7(1)				
					1	Ni11	267.0(1)				

(*continued*)

TABLE 3 (*continued*)

Ni3	1 Ni5	244.8(1)	Ni8	1 Ce1	306.4(1)	C2	1 Ni3	194.6(7)
	1 Ni13	246.5(1)	Ni9	1 C1	191.9(9)		1 Ni14	195.6(6)
	1 Ni14	247.0(1)		2 Ni8	230.7(1)		1 Ni14	199.0(6)
	1 Ni3	251.5(1)		2 Ni1	240.7(1)			
	1 Ni4	256.1(1)		1 Ni12	243.4(2)			
	1 Ni1	260.9(1)		2 Ni6	257.8(1)			
	1 Ni5	264.6(1)		2 Ni7	259.4(1)			
	1 Ni11	265.4(1)		1 Ni10	269.5(2)			
	1 Ni10	273.5(1)		1 Ni11	297.0(2)			
	1 Ce2	298.3(1)		1 Ce2	302.6(1)			
	1 Ce1	308.2(1)	Ni10	1 Ni13	251.0(1)			
Ni4	1 C2	191.5(6)		1 Ni11	251.0(2)			
	1 Ni15	240.2(1)		2 Ni8	258.4(1)			
	1 Ni5	241.5(1)		2 Ni5	259.1(1)			
	1 Ni14	250.6(1)		2 Ni14	266.0(1)			
	1 Ni5	253.5(1)		2 Ni6	266.5(1)			
	1 Ni2	254.4(1)		1 Ni9	269.5(2)			
	1 Ni3	256.1(1)		2 Ni3	273.5(1)			
	1 Ni7	264.0(1)		1 Ce2	278.0(1)			
	1 Ni6	269.4(1)						
	1 Ni7	269.7(1)						
	1 Ni4	269.9(1)						
	1 Ce2	301.6(1)						
	1 Ce1	306.5(1)						

[a] All distances shorter than 440 pm (Ce–Ce, Ce–Ni, C–C), 332 pm (Ni–Ni), 303 pm (Ce–C) and 250 pm (Ni–C) are listed.

(coordination number 5). Normally the carbon atoms have octahedral or trigonal prismatic coordinations (coordination number 6) in such compounds. In the anion $[Ni_6(CO)_{12}]^{2-}$ the shortest Ni–C distance is 175 pm [16].

It is remarkable that both carbon atoms in $Ce_2Ni_{22}C_{3-x}$ have no cerium neighbours (Fig. 4).Usually the carbon atoms in such ternary carbides have at least one lanthanoid or actinoid neighbour. Two other exceptions occur in the structures of $La_2Ni_5C_3$ [17] and $Th_3Ni_5C_5$ [18]. Both of these structures contain one octahedral carbon site with six nickel neighbours at average Ni–C distances of 192.4 pm and 184.5 pm respectively. For the trigonal prismatic C2 atom in $Ce_2Ni_{22}C_{2.75}$ the average Ni–C distance is 193.9 pm.

It has already been mentioned that the cell volume and the electrical resistivity behaviour of the cerium compound suggest mixed or intermediate valence. This can also be concluded from a comparison of the coordination polyhedra of the Ce1 and Ce2 atoms. Normally the average distances increase with increasing coordination number. Here this is also the case; however, the difference in the average interatomic distance is rather large: the Ce1 atom with 20 near nickel neighbours has an average Ce–Ni distance of 311.1 pm, while it is 307.1 pm for the Ce2 atom with coordination number 19. The difference is even more remarkable considering that the ten shortest Ce2–Ni distances of between 278 and 303 pm are all shorter than the shortest

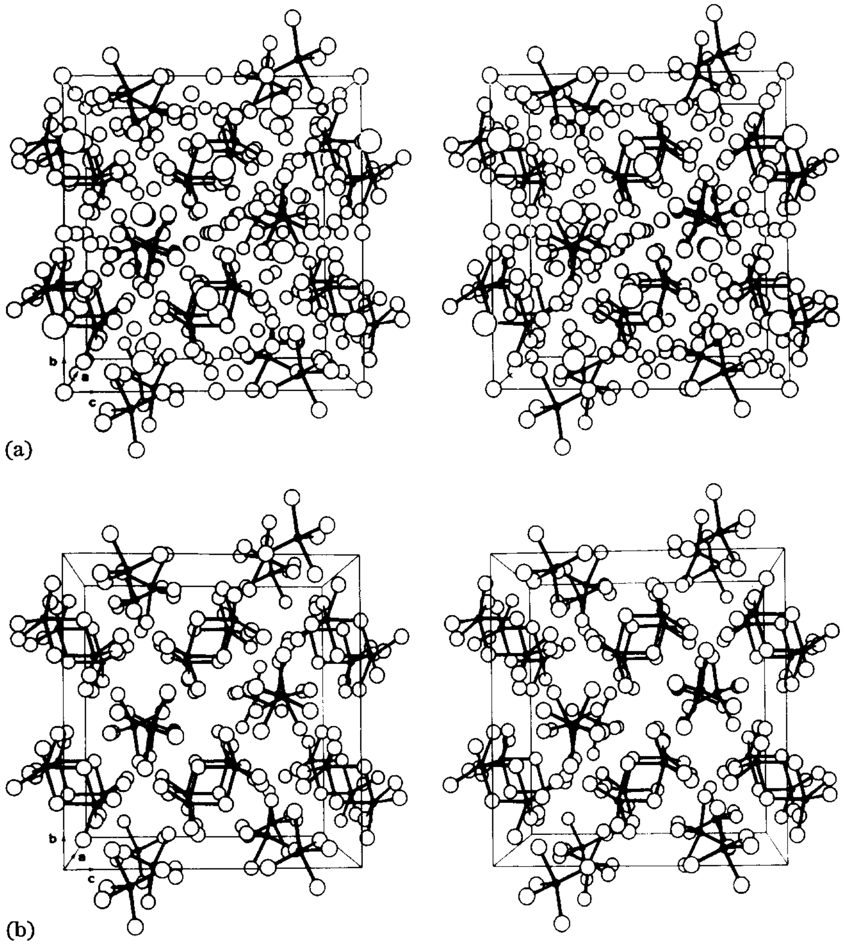

Fig. 3. Stereo plots of the $Ce_2Ni_{22}C_{3-x}$-type structure: (a) all atoms; (b) only those atoms with Ni–C bonds; ○, circles, cerium atoms; ○, nickel atoms; ●, carbon atoms.

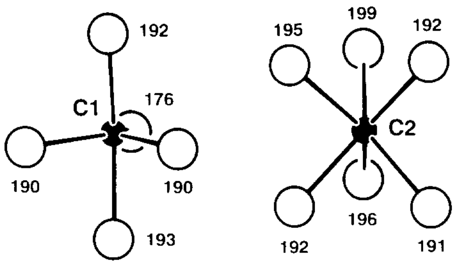

Fig. 4. Atomic environments of the carbon atoms in $Ce_2Ni_{22}C_{3-x}$.

Ce1–Ni distance of 306 pm. Thus, not only a dynamic intermediate valence of the cerium atoms (as suggested by the electrical resistivity behaviour) can be assumed, but also a static difference with the trivalent and tetravalent cerium atoms preferring the Ce1 and Ce2 sites respectively.

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