Y2¶	0.33485 (3)	0.12649 (5)	0.08416 (2)	0.0075 (2)
Ca3††	0	0.37890 (6)	1/4	0.0065 (2)
Y3‡‡	0	0.37890 (6)	1/4	0.0065 (2)
Si1	0.09475 (6)	0.07335 (11)	0.09901 (5)	0.0056 (2)
Si2	0.27403 (6)	0.37315 (11)	0.26967 (5)	0.0054 (2)
Si3	0.40206 (6)	0.18031 (11)	0.40679 (5)	0.0061 (2)
O1	0.0014 (2)	0.1754 (3)	0.13787 (14)	0.0114 (5)
O2	0.0630 (2)	0.1227 (3)	0.56374 (13)	0.0109 (4)
O3	0.1584 (2)	0.3787 (3)	0.29922 (14)	0.0132 (5)
O4	0.1588 (2)	0.1532 (3)	0.01777 (15)	0.0162 (5)
O5	0.1794 (2)	0.0447 (3)	0.17946 (14)	0.0114 (5)
O6	0.3048 (2)	0.3694 (3)	0.16674 (13)	0.0120 (5)
O7	0.3202 (2)	0.2041 (3)	0.32360 (13)	0.0105 (5)
O8	0.3352 (2)	0.1108 (3)	0.49013 (14)	0.0116 (5)
O9	0.5035 (2)	0.0737 (3)	0.12785 (14)	0.0133 (5)

† Site occupancy = 0.888 (3). ‡ Site occupancy = 0.111 (2). § Site occupancy = 0.538 (3). ¶ Site occupancy = 0.461 (2). †† Site occupancy = 0.145 (4). ‡‡ Site occupancy = 0.855 (4).

Table 2. *Selected geometric parameters (Å)*

Ca1/Y1—O6^{i}	2.301 (2)	Ca3/Y3—O3	2.228 (2)
Ca1/Y1—O1^{ii}	2.335 (2)	Ca3/Y3—O1	2.285 (2)
Ca1/Y1—O8^{iii}	2.538 (2)	Ca3/Y3—O1^{ii}	2.285 (2)
Ca1/Y1—O8	2.577 (2)	Ca3/Y3—O9^{vii}	2.352 (2)
Ca1/Y1—O7	2.582 (2)	Ca3/Y3—O9^{viii}	2.352 (2)
Ca1/Y1—O2	2.595 (2)	Si1—O1	1.582 (2)
Ca1/Y1—O4^{iv}	2.613 (2)	Si1—O4	1.600 (2)
Ca1/Y1—O3	2.619 (2)	Si1—O5	1.650 (2)
Ca2/Y2—O4^{v}	2.275 (2)	Si1—O2^{vi}	1.657 (2)
Ca2/Y2—O6	2.276 (2)	Si2—O6	1.578 (2)
Ca2/Y2—O8^{vi}	2.301 (2)	Si2—O3	1.604 (2)
Ca2/Y2—O9	2.370 (2)	Si2—O5^{vii}	1.644 (2)
Ca2/Y2—O4	2.547 (2)	Si2—O7	1.648 (2)
Ca2/Y2—O3^{i}	2.578 (2)	Si3—O9^{ix}	1.590 (2)
Ca2/Y2—O5	2.588 (2)	Si3—O8	1.616 (2)
Ca3/Y3—O3^{ii}	2.228 (2)		

Symmetry codes: (i) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $-x, y, \frac{1}{2}-z$; (iii) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (iv) $x, -y, \frac{1}{2}+z$; (v) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (vi) $x, -y, z-\frac{1}{2}$; (vii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (viii) $x-\frac{1}{2}, \frac{1}{2}+y, z$; (ix) $1-x, y, \frac{1}{2}-z$.

Data collection: *CONTROL* (Rigaku Corporation, 1992). Cell refinement: *CONTROL*. Data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ATOMS*2.0 (Dowty, 1991). Software used to prepare material for publication: *SHELXL*93.

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References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.

Dowty, E. (1991). *ATOMS*2.0. *A Computer Program for Displaying Atomic Structures.* IBM Version 2.0. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.

Fischer, K. (1969). *Z. Kristallogr.* **129**, 222–243.

Hilmer, W. (1963). *Sov. Phys. Crystallogr.* **7**, 537–576.

Ito, J. (1968). *Am. Mineral.* **53**, 890–907.

Molecular Structure Corporation (1992). *TEXSAN. TEXRAY Structure Analysis Package.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

O'Keeffe, M. & Hyde, B. G. (1981). *Structure and Bonding in Crystals*, Vol. 1, edited by M. O'Keeffe & A. Navrotsky, pp. 227–254. New York: Academic Press.

Rigaku Corporation (1992). *CONTROL.* Program set V. Rigaku Corporation, Tokyo, Japan.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Wanmaker, W. L., Vrugt, J. W. & Verlijsdonk, J. G. (1971). *Philips Res. Rep.* **26**, 373–381.

Warshaw, I. & Roy, R. (1962). *Inorg. Chem.* **1**, 719–720.

Yamanaka, T. & Mori, H. (1981). *Acta Cryst.* B**37**, 1010–1017.

Yamane, H., Nagasawa, T., Shimada, M. & Endo, T. (1997). *Acta Cryst.* C**53**, 1367–1369.

Acta Cryst. (1997). C**53**, 1536–1538

Zirconium–Nickel, Zr_7Ni_{10}: Space Group Revision for the Stoichiometric Phase

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Abstract

The intermetallic compound Zr_7Ni_{10} is a structure-type representative which was previously reported to crystallize in the non-centrosymmetric space group *Aba*2. In the present work we show that the correct space group is centrosymmetric *Cmca*.

Comment

On the basis of metallographic data, Kirkpatrick & Larsen (1961) assigned the intermetallic phase Zr_7Ni_{10} a homogeneity range extending from 56.3 to 58.9 at.% Ni. In a separate investigation, Kirkpatrick, Smith & Larsen (1962) investigated its crystal structure as a function of composition and found that the nickel-

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rich phase (referred to as stoichiometric) crystallized in the non-centrosymmetric space group *Aba*2 and the zirconium-rich phase in the centrosymmetric space group *Pbca*. Their work was based on photographic data (Weissenberg and precession photographs).

Both structures were the first of their types and subsequently used as structure-type representatives in crystal-data compilations (see for example, Villars & Calvert, 1991). In the database of crystal structure types compiled by Parthé *et al.* (1993), the authors noticed that the stoichiometric phase had a pseudo-centrosymmetric atom arrangement, but a careful analysis showed that at least one atom site broke inversion symmetry to a significant extent. Since the authors of the original structure work had considered the possibility of inversion symmetry during their data analysis and reached a negative conclusion, it remained unclear if their space group assignment was correct or biased by the possible low quality of the data.

In the present work, we demonstrate that the true space group of the so-called stoichiometric phase of Zr_7Ni_{10} is *Cmca*. As shown in Fig. 1, the structure is composed of pseudo-tetragonal buckled layers ($b \simeq c$, $x_{Ni1} + x_{Ni2} \simeq 1/2$, $y_{Ni1} \simeq z_{Ni2}$, $y_{Ni2} + z_{Ni1} \simeq 1/2$, $y_{Ni3} + z_{Ni3} \simeq 1/2$, $y_{Zr1} + z_{Zr1} \simeq 1/2$, $y_{Zr2} \simeq 1/4$) which are stacked along the *a* axis.

The interatomic distances between Zr and its nearest Ni neighbours (2.60–2.75 Å) are significantly shorter than the sum of the metallic radii (2.84 Å), thus indicating strong Zr—Ni interactions. The Ni—Ni distances (2.62–2.63 Å) are longer than, and the Zr—Zr distances (3.19–3.35 Å) similar to, the sum of metallic radii (Ni—Ni 2.48, Zr—Zr 3.20 Å).

The compound is of technological interest because of its hydrogen-absorption properties and its possible hydrogen-storage applications (Joubert, Latroche & Percheron-Guégan, 1995). Moreover, its presence in the form of precipitates in Laves phase hydriding alloys was shown to improve the electrochemical properties of nickel metal hydride batteries (Joubert, Latroche, Percheron-Guégan & Bouet, 1996).

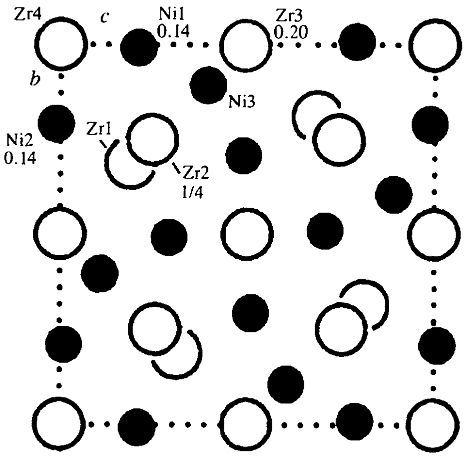

Fig. 1. Structural projection of orthorhombic Zr_7Ni_{10} along the *a* axis showing the pseudo-tetragonal symmetry of the layers ($x = 0$ unless indicated otherwise).

Finally, the crystal structures of Zr_7Cu_{10}, Hf_7Ni_{10} and Hf_7Cu_{10}, which were reported to be isotypic with Zr_7Ni_{10} (Kirkpatrick, Smith & Larsen, 1962; Bsenko, 1975) may also have a centrosymmetric atom arrangement, and thus should be reinvestigated.

Experimental

The alloy was synthesized from the elements by induction melting in a copper cooled crucible under high vacuum, annealing at 1273 K for 1 month (with the alloy wrapped in tantalum foil in a silica tube) under high vacuum and at 1413 K for 4 days under an argon atmosphere. The composition obtained by electron-probe microanalysis was $Zr_{7.1(2)}Ni_{9.9(2)}$. A single crystal was found in the crushed alloy.

Crystal data

Zr_7Ni_{10}
$M_r = 1225.5$
Orthorhombic
Cmca
$a = 12.381\,(10)$ Å
$b = 9.185\,(5)$ Å
$c = 9.221\,(5)$ Å
$V = 1048.6\,(11)$ Å^3
$Z = 4$
$D_x = 7.762$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 8.63$–$28.77°$
$\mu = 24.03$ mm^{-1}
$T = 293$ K
Parallelepiped
$0.077 \times 0.051 \times 0.016$ mm
Metallic silver

Data collection

Philips PW1100 diffractometer
ω–2θ scans
Absorption correction: analytical correction from measured crystal shape (indexed faces) and size according to Blanc, Schwarzenbach & Flack (1991)
$T_{min} = 0.490$, $T_{max} = 0.678$
3710 measured reflections

799 independent reflections
720 reflections with $F^2 > 0$
$R_{int} = 0.052$
$\theta_{max} = 29.99°$
$h = -17 \rightarrow 17$
$k = -12 \rightarrow 12$
$l = -12 \rightarrow 12$
2 standard reflections frequency: 60 min intensity decay: 1.25%

Refinement

Refinement on F^2
$R(F) = 0.061$
$wR(F^2) = 0.038$
$S = 1.289$
720 reflections
46 parameters
$w = 1/[\sigma^2(F^2) + 0.06F^2]$
$(\Delta/\sigma)_{max} = 0.00012$
$\Delta\rho_{max} = 3.69$ e Å^{-3}
$\Delta\rho_{min} = -3.82$ e Å^{-3}

Extinction correction: secondary extinction with Gaussian distribution according to Becker & Coppens (1974)
Extinction coefficient: 4300 (100)
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ni1	0.14438 (8)	0.01115 (12)	0.20822 (9)	0.0118 (2)
Ni2	0.35507 (8)	0.29157 (9)	0.00833 (14)	0.0120 (2)
Ni3	0	0.10755 (16)	0.39423 (18)	0.0142 (4)
Zr1	0	0.31219 (12)	0.18847 (13)	0.0135 (3)
Zr2	1/4	0.25466 (12)	1/4	0.0041 (2)
Zr3	0.30634 (8)	0	0	0.0097 (2)
Zr4	0	0	0	0.0078 (3)

The refined lattice parameters agree to within 3σ with the results of Kirkpatrick, Smith & Larsen (1962). The precision achieved (10^{-3}) is typical for a laboratory diffractometer and crystals of intermetallic compounds. Most differences of the positional parameters in the non-centrosymmetric model from their associated positions in the centrosymmetric model are less than 6σ. Only Ni2 (which splits into two atoms in the non-centrosymmetric model) differs by 20σ in x and 15σ in z. However, the displacement ellipsoid of Ni2 is quite isotropic. The origin shift between the model in *Cmca* and the model in *Aba*2 is −0.693, 1/2, 1/2. The transformation is c, $-b$, a. The non-centrosymmetric model shows some very short distances (Zr—Ni = 2.38 Å, Ni—Ni = 2.15 Å). The residual in the electron density map and the inhomogeneous equivalent isotropic displacement parameters of the Zr atoms are probably due to the small size of the crystal and difficulty in correctly indexing all faces to determine the shape of the crystal.

Data collection: PW1100 software (Philips, 1974). Cell refinement: *LATCON* in *Xtal*3.2 (Hall, Flack & Stewart, 1992). Data reduction: *REFCAL* and *SORTRF* in *Xtal*3.2. Program(s) used to refine structure: *LSLS* in *Xtal*3.2. Software used to prepare material for publication: *BONDLA* and *CIFIO* in *Xtal*3.2. Structure tidying routines: Gelato & Parthé (1987).

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References

Becker, P. J. & Coppens, P. (1974). *Acta Cryst.* A**30**, 129–147.

Blanc, E., Schwarzenbach, D. & Flack, H. D. (1991). *J. Appl. Cryst.* **24**, 1035–1041.

Bsenko, L. (1975). *J. Less-Common Met.* **40**, 365–366.

Gelato, L. M. & Parthé, E. (1987). *J. Appl. Cryst.* **20**, 139–143.

Hall, S. R., Flack, H. D. & Stewart, J. M. (1992). Editors. *Xtal*3.2 *Reference Manual*. Universities of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.

Joubert, J.-M., Latroche, M. & Percheron-Guégan, A. (1995). *J. Alloys Compd.* **231**, 494–497.

Joubert, J.-M., Latroche, M., Percheron-Guégan, A. & Bouet, J. (1996). *J. Alloys Compd.* **240**, 219–228.

Kirkpatrick, M. E. & Larsen, W. L. (1961). *Trans. Am. Soc. Met.* **54**, 580–590.

Kirkpatrick, M. E., Smith, J. F. & Larsen, W. L. (1962). *Acta Cryst.* **15**, 894–903.

Parthé, E., Gelato, L., Chabot, B., Penzo, M., Cenzual, K. & Gladyshevskii, R. (1993). *TYPIX. Standardized Data and Crystal Chemical Characterization of Inorganic Structure Types*. In *Gmelin Handbook of Inorganic and Organometallic Chemistry*. Heidelberg: Springer-Verlag.

Philips (1974). *PW*1100 *Users Manual*. Philips Scientific and Analytical Equipment, Eindhoven, The Netherlands.

Villars, P. & Calvert, L. D. (1991). *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*. Ohio: ASM International.