

centre of the ring and perpendicular to the molecular plane.

Computations

All the calculations were carried out using the IBM 360/75 computer at Mitsubishi Computer Centre and the MELCOM 9100 computer in our laboratory. Calculations of $|F_o|$ and $|F_c|$, Fourier syntheses, diagonal least-squares and block-diagonal least-squares analyses, bond lengths, bond angle and best plane calculations were carried out by *RDTR-3*, *RSSF-4*, *RSDLS-3*, *HBL-IV*, *RSDA-4* and *RSBP-3* of UNICS computer program system respectively (Crystallographic Society of Japan, 1967). The program for computation of dihedral angles was *BOND* written by Iitaka. Thermal ellipsoids were plotted by the *ORTEP* program written by Johnson (1965).

The authors thank Dr T. Haga for kindly supplying crystals.

References

- BERNDT, A. F. & MARSH, R. E. (1963). *Acta Cryst.* **16**, 118.
 CHAIWASIE, S. & FENN, R. H. (1968). *Acta Cryst.* **B24**, 525.
 EVRARD, P. G., PIRET, P., GERMAIN, G. & VAN MEERSSCHE, M. (1971). *Acta Cryst.* **B27**, 661.
 FERGUSON, G. & SIM, G. A. (1961). *Acta Cryst.* **14**, 1262.
 HAGA, T. (1969). Japan Patent 574642.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
 KURAHASHI, M., FUKUYO, M. & SHIMADA, A. (1967). *Bull. Chem. Soc. Japan*, **40**, 1296.
 LIEBLING, G. & MARSH, R. E. (1965). *Acta Cryst.* **19**, 202.
 SAKORE, T. D., TAVALE, S. S. & PANT, L. M. (1967). *Acta Cryst.* **22**, 720.
 WHITLA, W. A., POWELL, H. M. & VENANZI, L. M. (1966). *Chem. Commun.* p. 310.
 WILSON, F. C. & SHOEMAKER, D. P. (1957). *J. Chem. Phys.* **27**, 809.
 ZIEGLER, M. (1967). *Z. anorg. allg. Chem.* **355**, 12.

Acta Cryst. (1972). **B28**, 1594

The Structure of Zr_2Ni_7 *

BY F. R. ESHELMAN AND J. F. SMITH

Institute for Atomic Research and Department of Metallurgy, Iowa State University, Ames, Iowa 50010, U.S.A.

(Received 13 September 1971)

Zr_2Ni_7 has been found to crystallize with monoclinic symmetry: $a = 4.698 \pm 0.009$, $b = 8.235 \pm 0.013$, $c = 12.193 \pm 0.016$ Å, and $\beta = 95.83 \pm 0.13^\circ$. The crystal structure, with $C2/m$ space group symmetry, is compatible with observed intensities of X-ray reflections. The unit cell contains four formulae of Zr_2Ni_7 . An R index of 0.091 was obtained from three-dimensional intensity data totaling 2031 independent reflections. The intensity data were accumulated diffractometrically with the θ - 2θ scan technique. Zirconium atoms occur in two independent sets, each with coordination number 16. The coordination atmospheres of the independent zirconium atoms are remarkably similar, with geometries related to Laves-Friauf polyhedra. Nickel atoms occur in four independent sets, each with coordination number 12. The coordination atmospheres of each of two pairs of independent nickel atoms are closely comparable, but differ between pairs. Nickel coordination atmospheres can for both pairs be considered as irregular icosahedra; however, the irregularity for one pair of the coordination icosahedra is so severe that two adjacent faces are coplanar to within the precision of the structure determination. Thus, this coordination polyhedron is not truly an icosahedron but has only 19 faces.

Introduction

Kirkpatrick & Larsen (1961) have examined the phase relationships in the zirconium-nickel binary system across the complete composition range and have reported the existence of seven intermediate phases: Zr_2Ni , $ZrNi$, Zr_7Ni_{10} , Zr_9Ni_{11} , Zr_2Ni_5 , Zr_2Ni_7 , and $ZrNi_5$. The crystal structures of Zr_2Ni and $ZrNi$ have been determined by Kirkpatrick, Bailey & Smith (1962), the structure of Zr_7Ni_{10} has been determined by

Kirkpatrick, Smith & Larsen (1962), and the structure of $ZrNi_5$ has been determined by Smith & Guard (1957).

Crystallographic data on the three remaining compounds are incomplete and must be considered tentative; these data include a limited amount of symmetry information and some values for lattice parameters. In the particular case of Zr_2Ni_7 , Kirkpatrick & Larsen (1961) found that attempts to isolate single crystals of the phase by mechanical means always resulted in plastic deformation. Diffraction patterns from crystals they were able to obtain were indicative of a layered structure, and rough values for orthogonal

* Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission. Contribution No. 3091.

lattice parameters in the plane of the layers were determined as $a \sim 4.8 \text{ \AA}$ and $b \sim 8.1 \text{ \AA}$.

Multiple-splitting of all observed reflections with l other than zero made it impossible to completely establish the unit-cell dimensions. Subsequent observations at this laboratory on arc-melted alloys with compositions in the vicinity of Zr_2Ni_7 confirm that these alloys will tolerate some plastic deformation, with the behavior of the alloys being characterized as tough rather than brittle. The present investigation was undertaken in order to complete the determination of the crystal structure of Zr_2Ni_7 .

Procedure and results

Zirconium was obtained from Westinghouse Atomic Corp., with the supplier's analysis indicating the following impurities in p.p.m. by weight: nitrogen, <5; carbon, 43; aluminum, <35; titanium, 42; magnesium, <10; and iron, 90. Nickel was supplied by the Belton Smelting and Refining Works, with an analysis, again in p.p.m. by weight: carbon, 100; copper, 10; iron, 70; and sulfur, 20. Weights corresponding to 79 at.% nickel and 21 at.% zirconium were arc-melted under inert atmosphere with a non-consumable tungsten electrode. Mixing of the elemental components was facilitated by repeated arc melting, with the solidified sample being inverted between each successive melting. The phase diagram shows Zr_2Ni_7 to melt congruently, so in alloys near this composition, Zr_2Ni_7 forms at first solidification.

In many alloys the intermetallic phases are sufficiently brittle that small crystals suitable for structure analyses may be obtained by mechanical fragmentation. In the present instance, attempts to obtain crystals in this way always produced plastic deformation in the crystals. Suitable crystals were isolated, however, by suspending pieces of alloy in a solution containing 10% nitric acid and 5% acetic acid. After a period of

reaction with the acid, particles were observed to drop free of the samples. These particles were filtered from the acid solution and were washed and dried. Individual crystals, in the form of thin platelets with irregular outlines, could be manually separated from the filtered residue under low-power optical magnification.

Precession photographs were taken from three different crystals. All three crystals could be indexed on the basis of the same monoclinic unit cell. The general extinction of reflections with $h+k$ odd indicated space group $C2$, Cm , or $C2/m$. One crystal was chosen for the accumulation of intensity data, and precision lattice parameters were determined for this crystal. Twenty-two reflections in the range $98^\circ < 2\theta < 139^\circ$ were scanned using a General Electric single-crystal orienter with molybdenum radiation. An extrapolation against the Nelson & Riley (1945) function using values (Cullity, 1956) of 0.70926 and 0.713543 \AA for the wavelengths of $K\alpha_1$ and $K\alpha_2$, respectively, was accomplished

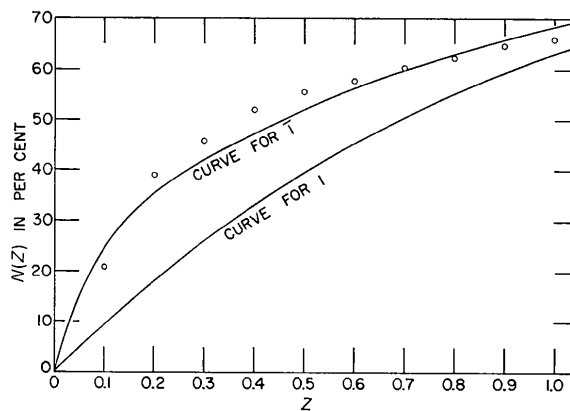


Fig. 1. Intensity statistics for Zr_2Ni_7 . $N(z)$ is the relative number of reflections with intensity less than or equal to the function z of the local average intensity. The solid lines represent theoretical distributions.

Table 2. Structural parameters for Zr_2Ni_7 in space group $C2/m$

(a) Positional parameters

Set		x	y	z
4(i)	Zr(1)	0.2115 ± 0.0007	0	0.6133 ± 0.0003
4(i)	Zr(2)	0.2695 ± 0.0007	0	0.8840 ± 0.0003
4(i)	Ni(1)	0.2561 ± 0.0011	0	0.2460 ± 0.0004
8(j)	Ni(2)	0.2075 ± 0.0007	0.1625 ± 0.0005	0.0762 ± 0.0003
8(j)	Ni(3)	0.2974 ± 0.0006	0.1679 ± 0.0004	0.4208 ± 0.0002
8(j)	Ni(4)	0.5033 ± 0.0007	0.2464 ± 0.0007	0.2507 ± 0.0003

(b) Temperature factors (β 's $\times 10^4$)

Anisotropic temperature factors of the form $T = \exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{13}hl + 2\beta_{23}kl + 2\beta_{12}hk)$.

Set		β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
4(i)	Zr(1)	4 ± 8	8 ± 3	2 ± 1	0	-3 ± 2	0
4(i)	Zr(2)	9 ± 9	15 ± 4	12 ± 2	0	6 ± 3	0
4(i)	Ni(1)	34 ± 7	15 ± 2	8 ± 1	0	9 ± 2	0
8(j)	Ni(2)	53 ± 8	34 ± 4	12 ± 1	6 ± 5	5 ± 3	1 ± 2
8(j)	Ni(3)	65 ± 8	15 ± 3	7 ± 1	10 ± 4	4 ± 3	2 ± 1
8(j)	Ni(4)	33 ± 4	16 ± 2	12 ± 1	-3 ± 2	4 ± 1	0 ± 1

analytically with a least-squares fit. The following lattice parameters were obtained: $a=4.698 \pm 0.009$, $b=8.235 \pm 0.013$, $c=12.193 \pm 0.016$ Å, and $\beta=95.83 \pm 0.13^\circ$.

The intensity data were taken with filtered Mo $K\alpha$ radiation and a nonautomated General Electric diffractometer fitted with a single-crystal orienter and a scintillation counter. The θ - 2θ scan technique was employed. 2031 independent reflections with $2\theta \leq 90^\circ$ were counted at a scan rate for 2θ of 2°min^{-1} . Reflections with $2\theta < 60^\circ$ were given an 83.3 sec (2.78°) scan, while those with $2\theta \geq 60^\circ$ were scanned for 100 sec (3.33°). The reflections were traced simultaneously as they were counted. Background counts were made behind the reflection for the same period of time as the scan. If the trace of the reflection indicated a different background in front than behind the reflections, the background was also counted at the lower angle and the mean background was used for obtaining the reflection intensity. The 400, 0,12,0, and 0,0,12 reflections were used as reference peaks and were monitored at the beginning and end of each period of data accumulation. In no case was the drift in intensity of any of these three reference reflections as much as one standard deviation.

Standard corrections were made for Lorentz and polarization effects. The crystal used for the accumulation of intensity data was approximately $0.37 \times 0.15 \times 0.014$ mm. Photomicrographs were taken of the crystal, from which the geometric shape of the crystal was approximated by 22 planes. This geometric approximation was combined with a linear absorption factor of 312 cm^{-1} , and the computer program of Busing & Levy (1957) was used to compute absorption corrections. Transmission factors were found to vary by a factor of about 50, ranging from 0.0038 and 0.0092 for

the 020 and 040 reflections to 0.511 and 0.496 for the 0,2,15 and 0,0,14 reflections, respectively.

A statistical analysis of the intensity data by the method of Howells, Phillips & Rogers (1950) indicated the centrosymmetric space group $C2/m$. A graph of this analysis is shown in Fig. 1. Comparison of the atomic volumes with the volume of the unit cell indicated a high probability that the stoichiometry Zr_2Ni_7 was correct with four formula weights per unit cell. A three-dimensional Patterson map was constructed, and examination of this map indicated the presence of six imperfect layers, with layering normal to the c axis. The nature of the $P(xy0)$ and $P(x, y, \frac{1}{8})$ sections showed that the layering in this structure was similar to the layering in the monoclinic PuNi_4 structure (Cromer & Larson, 1960). A trial structure was postulated in the centrosymmetric space group on the basis of the composite evidence. This trial structure refined satisfactorily with the least-squares program of Busing, Martin & Levy (1962). Atomic scattering factors and anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography* (1962), and final refinement was based on a full matrix and included anisotropic temperature factors. With unit weights, the final refinement resulted in a residual, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, of 0.087 for 1009 observed reflections and 0.091 for the total of 2031 observed and unobserved reflections. Other weighting schemes were tested, but none produced a significantly better value for the residual. The criterion of Larson & Cromer (1967) was utilized to evaluate the limit of observability. A comparison of calculated and observed structure factors is shown in Table 1. The final positional and thermal parameters are listed in Table 2. Coordination distances are listed in Table 3. Coordination geometries are illustrated in Fig. 2.

Table 3. *Interatomic distances in Zr_2Ni_7*

			Standard deviations are ~ 0.01 Å.					
	No.	Distance		No.	Distance		No.	Distance
Zr(1) to Zr(1)	1	3.24 Å	Ni(1) to Zr(1)	1	2.89 Å	Ni(3) to Zr(1)	1	2.79 Å
Zr(2)	1	3.28	Zr(1)	1	2.92	Zr(1)	2	2.76
Ni(1)	1	2.89	Zr(2)	1	2.80	Zr(1)	1	2.77
Ni(1)	1	2.92	Zr(2)	1	2.86	Ni(1)	1	2.53
Ni(3)	2	2.79	Ni(2)	2	2.46	Ni(3)	1	2.77
Ni(3)	4	2.76	Ni(3)	2	2.53	Ni(3)	1	2.57
Ni(3)	2	2.77	Ni(4)	2	2.34	Ni(3)	2	2.71
Ni(4)	2	2.87	Ni(4)	2	2.41	Ni(3)	1	2.44
Ni(4)	2	2.91	Ni(2) to Zr(2)	1	2.74	Ni(4)	1	2.46
Zr(2) to Zr(1)	1	3.28	Zr(2)	1	2.80	Ni(4)	1	2.48
Zr(2)	1	3.38	Zr(2)	1	2.70	Ni(4) to Zr(1)	1	2.87
Ni(1)	1	2.86	Zr(2)	1	2.82	Zr(1)	1	2.91
Ni(1)	1	2.80	Ni(1)	1	2.46	Zr(2)	2	2.88
Ni(2)	2	2.74	Ni(2)	1	2.68	Ni(1)	1	2.34
Ni(2)	2	2.80	Ni(2)	1	2.55	Ni(1)	1	2.41
Ni(2)	2	2.70	Ni(2)	2	2.76	Ni(2)	1	2.52
Ni(2)	2	2.82	Ni(2)	1	2.42	Ni(2)	1	2.54
Ni(4)	4	2.88	Ni(4)	1	2.52	Ni(3)	1	2.46
			Ni(4)	1	2.54	Ni(3)	1	2.48
						Ni(4)	2	2.35

Discussion

The Zr_2Ni_7 structure is efficiently packed, and the volume contraction that accompanies phase formation from the constituent elements is calculated to be 4.7%. The atomic array is pseudohexagonal normal to the a and b axes, and the layering along this pseudohexagonal axis is related to a number of other structures, particularly the cubic $MgCu_2$ and UNi_5 structures. Each zirconium atom in the Zr_2Ni_7 structure is coordinated to 2 other zirconium atoms and to 14 nickel atoms, for a total coordination of 16. The coordination atmospheres for the two independent zirconium atoms are remarkably similar, as evident in Fig. 2. Sixteen-fold coordinations are also found for the large atoms in the $MgCu_2$ - and UNi_5 -type structures, though in the

$MgCu_2$ structure the large atoms are coordinated to 4 other large atoms and to 12 small atoms, while in the UNi_5 structure each large atom is coordinated only to small atoms. In the $MgCu_2$ and UNi_5 structures the coordinations about the large atoms involve geometries known as Laves-Friauf polyhedra. The coordinations about zirconium atoms in Zr_2Ni_7 are quite similar except for the apical triads of atoms about the pseudohexagonal direction in Zr_2Ni_7 , which are rotated [as illustrated in Figs. 2(a) and 2(b)] approximately 30° from the orientation that would occur in true Laves-Friauf polyhedra. In Fig. 2 the vertical direction through Zr(1) and Zr(2) represents the pseudohexagonal axis and the perspectives are chosen to show the similarities in coordination. In the actual crystal structure the pseudohexagonal axes of Figs. 2(a) and

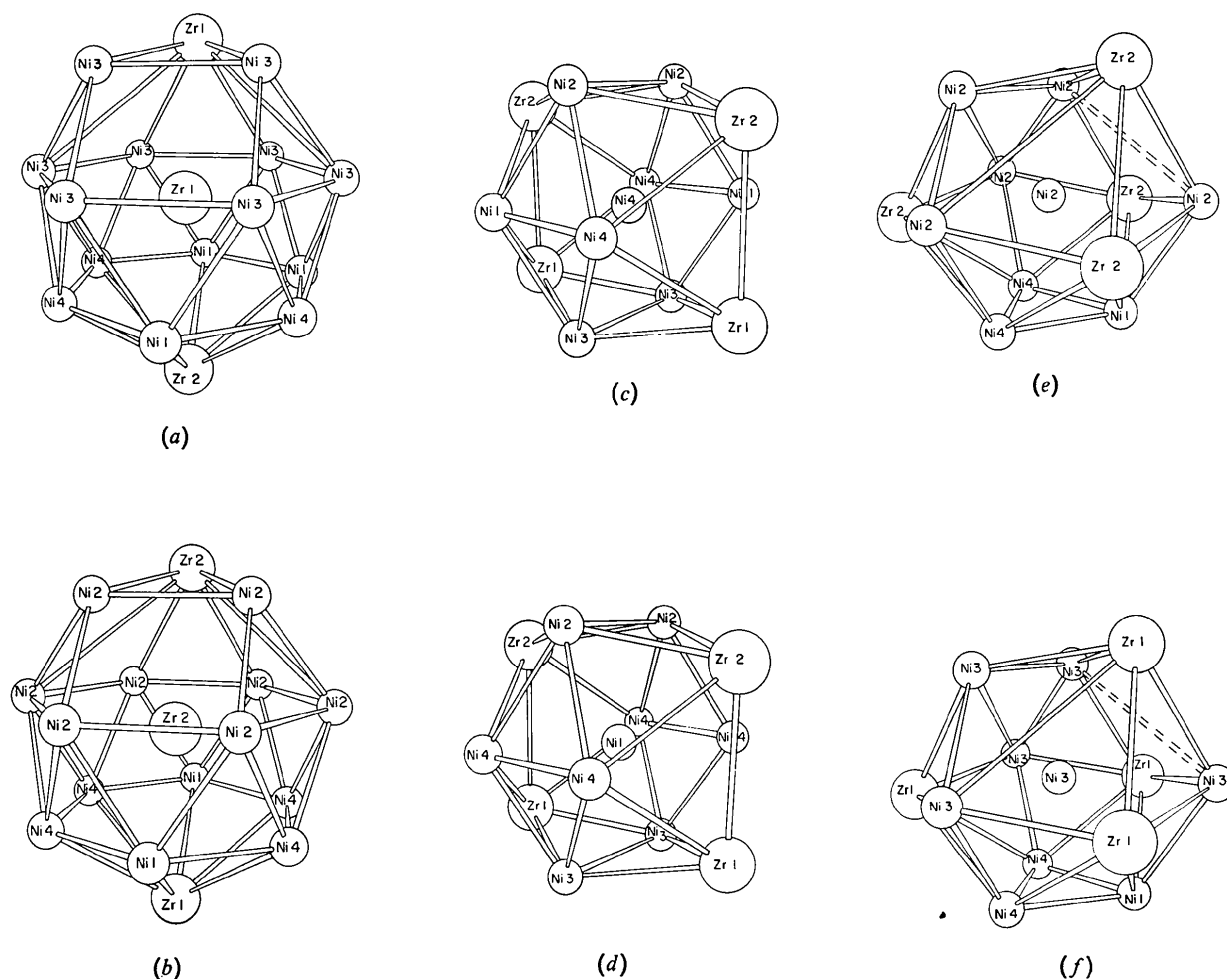


Fig. 2. Coordination atmospheres about (a) Zr(1), (b) Zr(2), (c) Ni(4), (d) Ni(1), (e) Ni(2), and (f) Ni(3). A striking similarity is evident in the coordinations about the pairs of independent atoms Zr(1) and Zr(2), Ni(1) and Ni(4), and Ni(2) and Ni(3). The vertical direction for all coordinations in this figure is the pseudohexagonal axis, and the coordinations for Zr(1), Ni(4), and Ni(2) are all viewed from the same crystallographic perspective so that in the crystal they share a common orientation. Relatively, the coordinations about Zr(2) and Ni(3) occur in the crystal with an opposite direction sense for the pseudohexagonal axis, while the coordination about Ni(1) in the crystal is rotated 60° about the pseudohexagonal axis with respect to the coordination about Ni(4). The dashed lines in (e) and (f) separate faces that are coplanar within experimental precision. These illustrations were generated with the computer program of Johnson (1965).

2(b) have opposite direction sense, and the lower portion of the coordination shell of Zr(2) interpenetrates the lower portion of the coordination shell of Zr(1).

Each nickel atom in Zr_2Ni_7 is coordinated to 4 zirconium atoms and to 8 other nickel atoms for a total coordination of 12. The total coordination about the small atoms in the $MgCu_2$ structure is also 12 and consists of 6 small atoms and 6 large atoms. In the UNi_5 structure the small atoms are of two types: one type is coordinated to 4 large atoms and 12 small atoms for a total coordination of 16 and with the coordination atmosphere involving a Laves-Friauf polyhedron, and the other type is coordinated to 3 large atoms and to 9 small atoms for a total coordination of 12. The twelvefold coordinations in all three structures are icosahedral or pseudo-icosahedral. In the Zr_2Ni_7 structure the coordinations about Ni(1) and Ni(4) and about Ni(2) and Ni(3) are nearly identical in each pair. However, the difference in the placements of the four coordinated zirconium atoms of Ni(1) and Ni(4), as compared to Ni(2) and Ni(3), generates significantly differing distortions from regularity between the polyhedral coordinations of the two pairs. In the case of the Ni(2) and Ni(3) coordinations, the irregularity is so severe that two adjacent trigonal faces of the pseudo-icosahedral coordinations are coplanar within the precision of the structure determination; thus, these coordinations are not truly icosahedra but are polyhedra with 19 faces.

In Fig. 2 the vertical direction for all of the coordination plots is the pseudohexagonal axis. The coordinations of Zr(1), Ni(4), and Ni(2) in Figs. 2(a), 2(c), and 2(e) are all viewed from the same crystallographic

perspective so that these three geometric arrangements share a common orientation in the actual crystal and differ only in translational position. In Fig. 2(d) the orientation of the Ni(1) coordination differs from that of the Ni(4) coordination in Fig. 2(c) by a 60° rotation about the pseudohexagonal axis, which is defined by the direction of the Zr(1)–Zr(2) bond. In the crystal structure this geometric relationship leads to a simple interpenetration of the coordination atmospheres of Ni(1) and Ni(4). In comparison, the orientation of the Ni(3) coordination in Fig. 2(f) is related to the orientation of the Ni(2) coordination in Fig. 2(e), in essentially the same manner as Zr(1) coordination is related to the Zr(2) coordination, and this relationship again leads to a simple interpenetration of the coordination atmospheres in the crystal structure.

A comparison of the $MgCu_2$, UNi_5 , and Zr_2Ni_7 structures is shown in Fig. 3. This figure illustrates, as Dwight (1961) has earlier pointed out, that selective substitution of small atoms for large atoms at alternating levels generates the UNi_5 structure from the $MgCu_2$ structure. The Zr_2Ni_7 structure cannot be similarly generated from the $MgCu_2$ or UNi_5 structures simply by atomic substitution, but it must also involve some deletion and displacement. In this sense, the relationship of the Zr_2Ni_7 structure to the UNi_5 structure is analogous to the relationship of the $PuNi_4$ structure to the $CaCu_5$ structure which has been noted by Cromer & Larson (1960). The Zr_2Ni_7 structure may conceptually be developed from either the $MgCu_2$ or UNi_5 structures, but since $ZrNi_5$ is isostructural with UNi_5 (Smith & Guard, 1957) it is more relevant to describe the latter. The $ZrNi_5$ structure is layered along

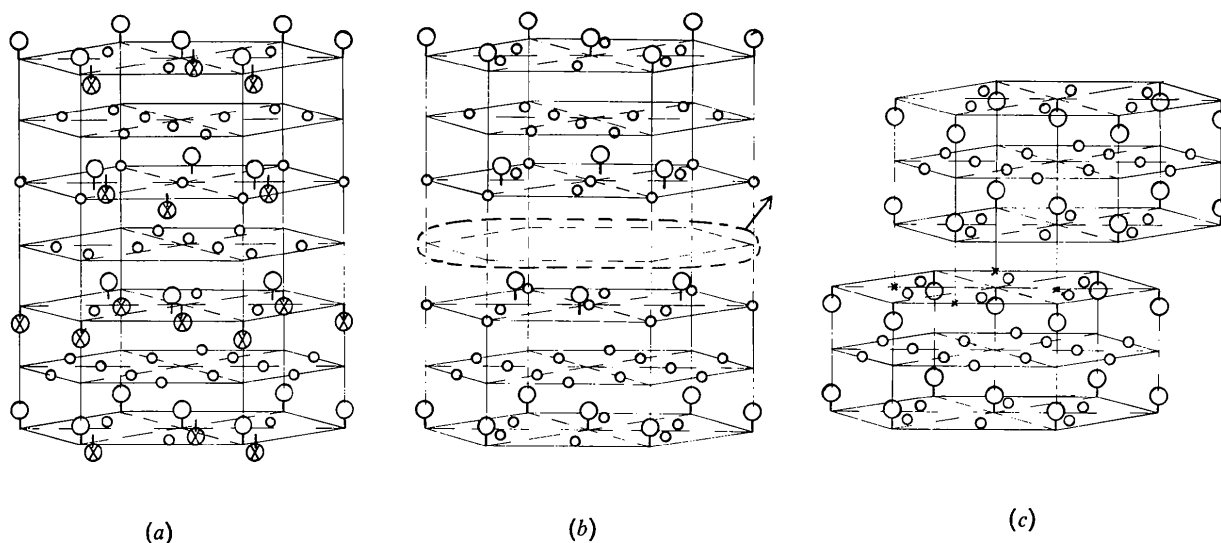


Fig. 3. Relationship of the Zr_2Ni_7 structure to the $ZrNi_5$ structure. (a) $ZrNi_5$ structure with the [111] direction normal to the layers. The large open circles, O, represent Zr atoms and the small open circles, o, and the large crossed circles, \otimes , represent Ni atoms. (Note: if the \otimes positions are occupied by the larger, rather than the smaller, species, this is the $MgCu_2$ structure.) (b) Alternate Ni layers have been removed and the Ni atoms at the \otimes positions have had their vertical displacement eliminated. (c) The alternate Zr layers have been inverted and realigned, and the upper structural motif has been displaced laterally and downward to produce the stacking arrangement of Zr_2Ni_7 .

the [111] direction and every 7th layer reproduces the first. Fig. 3 shows that if one chooses as the first layer a wrinkled zirconium–nickel plane, the Zr_2Ni_7 structure is developed by the following steps. First, the alternate coplanar layers of nickel atoms are deleted and in each of the wrinkled layers all nickel atoms are allowed to become coplanar. Next, the 3rd and 7th layers are inverted and displaced so that zirconium pairs are aligned along the [111] direction. This direction becomes an $a \times b$ direction of the Zr_2Ni_7 structure, and the operations to this stage have formed three-layer groupings which are the basic motif of the Zr_2Ni_7 structure. The first layer of the motif is a mixed layer of zirconium and nickel atoms with the zirconium atoms having a small upward displacement from the plane of the nickel atoms; the middle layer is a coplanar net of nickel atoms; the third layer is the same as the first but with the zirconium atoms displaced downward. The final operation in developing the Zr_2Ni_7 structure consists of lowering and aligning the upper of the two structural motifs so that the upper duplicates the lower in accord with twofold rotational symmetry about the b axis of the Zr_2Ni_7 structure.

Cromer & Larson (1959) have commented that the Ce_2Ni_7 structure, as well as the $CeNi_3$ and $PuNi_3$ structures (Cromer & Olsen, 1959), can be considered as being formed by combinations of the $MgCu_2$ -type and $CaCu_5$ -type structures. Buschow (1970) has noted that the β - Gd_2Co_7 -type structure (Bertaut, Lemaire & Schweizer, 1965) is simply a stacking variant of the Ce_2Ni_7 structure and, as such, may also be considered as being composed of a combination of $MgCu_2$ -type and $CaCu_5$ -type structures. These structures are therefore all closely related to the Zr_2Ni_7 structure. However, one significant difference is evident. In the $CeNi_3$, $PuNi_3$, Ce_2Ni_7 , β - Gd_2Co_7 , $PuNi_4$, and $CaCu_5$ -type structures, at least some of the larger atoms occur in coplanar layers with the smaller atoms. In contrast, no large atoms are coplanar with small atoms in the $MgCu_2$, $MgZn_2$, UNi_5 , or Zr_2Ni_7 -type structures. Thus there appears to be no way in which twinning of the Ce_2Ni_7 or β - Gd_2Co_7 structures could give rise to diffraction patterns consistent with the present monoclinic Zr_2Ni_7 structure. This is relevant because the apparent monoclinic symmetry reported by Florio, Baenziger & Rundle (1956) for Th_2Co_{17} and Th_2Fe_{17} has been explained by Johnson, Smith & Wood (1969) as arising from extensive twinning of Th_2Zn_{17} -type structures. Finally, it seems reasonable to conclude

that the same factor which causes $ZrNi_5$ to crystallize with the UNi_5 -type structure rather than with the $CaCu_5$ -type structure must also be responsible for causing Zr_2Ni_7 to crystallize as it does rather than with the Ce_2Ni_7 or β - Gd_2Co_7 structure.

The authors are deeply indebted to Mr D. M. Bailey for many constructive suggestions and for assistance in adapting and utilizing existing computer programs. Appreciation is also extended to Mr F. A. Schmidt for preparing the alloys. Comments from Dr Sten Samson concerning the polyhedral coordinations around the individual atoms are gratefully acknowledged.

References

- BERTAUT, E. F., LEMAIRE, R. & SCHWEIZER, J. (1965). *Bull. Soc. franç. Minér. Crist.* **88**, 580.
 BUSCHOW, K. H. J. (1970). *Acta Cryst.* **B26**, 1389.
 Busing, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180.
 Busing, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS. A Fortran Crystallographic Least-squares Program*. Report ORNL-TM-305. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
 CROMER, D. T. & LARSON, A. C. (1959). *Acta Cryst.* **12**, 855.
 CROMER, D. T. & LARSON, A. C. (1960). *Acta Cryst.* **13**, 909.
 CROMER, D. T. & OLSEN, C. E. (1959). *Acta Cryst.* **12**, 689.
 CULLITY, B. D. (1956). *Elements of X-ray Diffraction*, p. 464. Reading, Mass.: Addison-Wesley.
 DWIGHT, A. E. (1961). *Trans. Amer. Soc. Met.* **53**, 479.
 FLORIO, J. V., BAENZIGER, N. C. & RUNDLE, R. E. (1956). *Acta Cryst.* **9**, 367.
 HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1965). *ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
 JOHNSON, Q., SMITH, G. S. & WOOD, D. H. (1969). *Acta Cryst.* **B25**, 464.
 KIRKPATRICK, M. E., BAILEY, D. M. & SMITH, J. F. (1962). *Acta Cryst.* **15**, 252.
 KIRKPATRICK, M. E. & LARSEN, W. L. (1961). *Trans. Amer. Soc. Metals*, **54**, 580.
 KIRKPATRICK, M. E., SMITH, J. F. & LARSEN, W. L. (1962). *Acta Cryst.* **15**, 894.
 LARSON, A. C. & CROMER, D. T. (1967). *Acta Cryst.* **23**, 70.
 NELSON, J. B. & RILEY, D. P. (1945). *Proc. Phys. Soc.* **57**, 160.
 SMITH, E. & GUARD, R. W. (1957). *J. Metals*, **9**, 1189.