CRYSTAL STRUCTURE DETERMINATION OF THE INTERMEDIATE PHASES $Ni_{10}Zr_7$ AND $Ni_{10}Hf_7$

by

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Signatures have been redacted for privacy

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INTRODUCTION

The need for high temperature materials having low neutron capture cross-sections led to the early investigation of many zirconium binary alloy systems. Among these was the zirconium-nickel system studied by Hayes et al. (1953) who reported phase relationships for the zirconium-rich portion of the system. The phase relationships for the nickel-rich region of the system were studied by Pogodin and Skorobogatova (1954), Smith and Guard (1957) and Kramer (1959). Numerous intermediate phases were reported to exist in the system, but the compositions and structures of many of these phases were left in question.

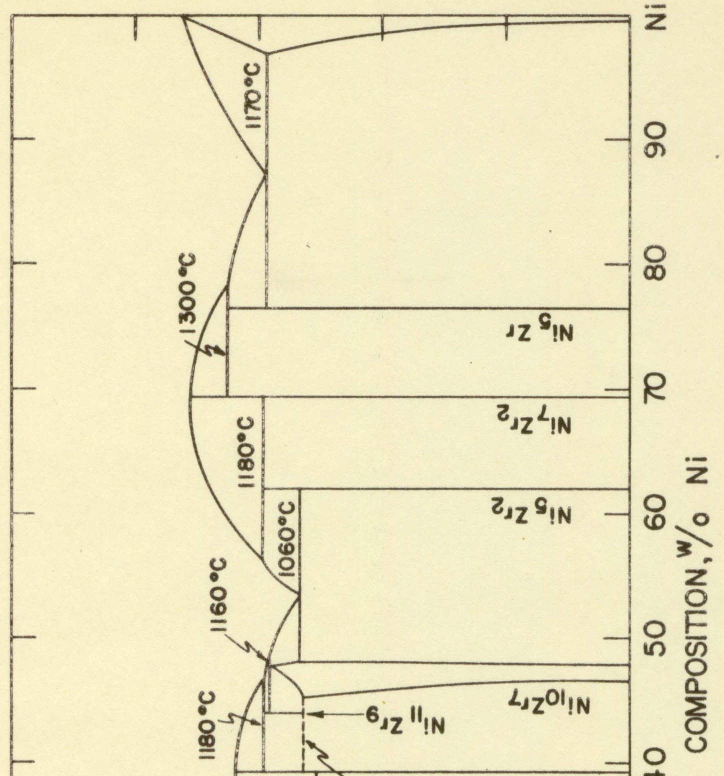
The intermediate phases of an alloy system usually have higher melting points and greater hardness than either of the pure elements. Therefore, an investigation of such phases could lead to high temperature materials which would have the desired properties for reactor application. For this reason, a study of several of the intermediate phases in the zirconium-nickel and hafnium-nickel systems was undertaken. Zirconium and zirconium-rich alloys have low neutron capture cross-sections which makes them especially useful in nuclear reactor core applications. Hafnium, on the other hand, has a large capture cross-section for neutrons and alloys containing substantial amounts of hafnium can be used as neutron absorbers or poisons for such things as reactor control rods and safety rods.

Since the chemical properties and elemental atomic diameters of hafnium and zirconium are similar, the intermediate phases which form between each of these elements and nickel would be expected to have similar stoichiometric ratios and crystal structures. Thus, if an intermediate phase in the zirconium-nickel system was found to have suitable nuclear, physical and chemical properties for reactor application, then the analogous hafnium phase having essentially the opposite nuclear properties would almost certainly be compatible with the similar chemical and physical environment.

The phase relationships of the zirconium-nickel alloy system were studied by Kirkpatrick (1959) and were found to be similar to those reported by Hayes et al. (1953) for the zirconium-rich portion of the phase diagram and those of Smith and Guard (1957) for the nickel-rich section of the diagram. The investigation of the area of the phase diagram between the intermediate phases NiZr and Ni_5Zr_2, which had not been investigated in detail previously, revealed the existence of the phases $Ni_{11}Zr_9$ and $Ni_{10}Zr_7$. The proposed phase diagram for the zirconium-nickel system is shown as Figure 1.

As can be seen from Figure 1, the intermediate phase $Ni_{10}Zr_7$ exhibits some solid solubility. The solubility limits of the phase were determined and it will be shown later that the range of solubility exists primarily on the zirconium-rich

Figure 1. The phase diagram for the nickel-zirconium alloy system


TEMPERATURE °C
2000
1600
1200
800
400
0
COMPOSITION, w/o Ni
Zr
10
20
30
40
50
60
70
80
90
Ni
960°C
840°C
1010°C
~1050°C
1180°C
1160°C
1060°C
1180°C
1300°C
1170°C
NiZr2
NiZr
Ni11Zr9
Ni10Zr7
Ni5Zr2
Ni7Zr2
Ni5Zr

side of stoichiometry and that the composition of the nickel-rich boundary is essentially that of stoichiometry. This solubility of zirconium in the phase produces a distortion in the crystal structure of the stoichiometric phase and a shift in symmetry as the composition varies from that of stoichiometry. The determination of the crystal structures for the stoichiometric and zirconium-rich compositions of the $Ni_{10}Zr_7$ phase and the stoichiometric $Ni_{10}Hf_7$ phase was undertaken and the details of these structures are presented herein. In referring to the various compositions of the $Ni_{10}Zr_7$ phase, the designation "stoichiometric phase" will refer to the phase having a composition equal to that of the nickel-rich phase boundary at 1060 °C, while the designation "zirconium-rich" will refer to the phase having a composition equal to that of the zirconium-rich phase boundary at 1030 °C.

EXPERIMENTAL PROCEDURE

Single crystal specimens of the compounds $Ni_{10}Zr_7$ and $Ni_{10}Hf_7$ were obtained from arc-melted alloys. The materials used in the preparation of these alloys were reactor-grade, crystal-bar zirconium, crystal-bar hafnium and Matthey spectrographically standardized nickel which was obtained from Johnson, Matthey and Co. Button-shaped ingots weighing between 30 and 50 grams were produced in a nonconsumable, tungsten electrode arc-furnace under an atomosphere of purified helium. Each alloy was inverted and remelted several times to promote homogeneity and then was cooled on a water-cooled copper hearth.

The preparation and isolation of single crystals of various compositions of the phases under investigation was based on the equilibrium diagram for the nickel-zirconium alloy system as shown in Figure 1. Zirconium-rich crystals of $Ni_{10}Zr_7$ used in the investigation were obtained from an alloy of 45.0 w/o Ni. The alloy was heated in a vacuum furnace to 1030 °C and held at this temperature for several hours. This treatment was followed by slow cooling to room-temperature. Crystals were isolated from the alloy by electrolytic etching in a solution of nitric acid, hydroflouric acid, ethylene glycol and water. The crystals obtained in this manner were elongated retangular prisms. A qualitative spectrographic analysis of representative crystals isolated in this manner indicated the presence of Cr, Cu, Fe and Si as trace impurities.

Crystals of the stoichiometric $Ni_{10}Zr_7$ phase were isolated from an alloy of 49.5 w/o Ni by heating the alloy specimen to a temperature just above the eutectic isotherm (≈ 1060 °C) and allowing gravitational separation of the eutectic liquid from the rigid network of primary crystals of $Ni_{10}Zr_7$. The crystals isolated from the upper surface of this partially melted alloy were similar in shape to the zirconium-rich crystals described above. A qualitative spectrographic analysis of representative crystals prepared in this manner also indicated the presence of Cr, Cu, Fe and Si as trace impurities. The concentrations of the trace impurity elements found in the stoichiometric crystals were not significantly different from those found in the zirconium-rich crystals. Crystals of the stoichiometric $Ni_{10}Hf_7$ phase were prepared by a method similar to that described for the stoichiometric $Ni_{10}Zr_7$ phase.

X-ray and photographic equipment used to collect the data were of standard design. Both precession and Weissenberg cameras were employed to obtain photographs of the reciprocal lattice. Preliminary photographs used to establish crystal symmetry and approximate cell dimensions were taken with both copper and molybdenum radiation. Intensity data for these structures were obtained through film methods. Due to the rather large errors in reflection intensities caused by absorption of copper radiation in nickel-zirconium crystals, only timed exposures taken with Mo Kα radiation were used for the determination of reflection intensities.

STRUCTURE OF THE ZIRCONIUM-RICH $Ni_{10}Zr_7$ PHASE

Symmetry and Cell Dimensions

Weissenberg photographs of the reciprocal lattice were obtained for all observed levels, k=0 through k=5, using Cu Kα radiation and rotating the crystal about the [010] axis. Precession photographs for the (hk0) through (hk3) and (0kℓ) through (4kℓ) levels were also taken with Mo Kα radiation. In every case the reciprocal lattice patterns exhibited $C_{2\ell}$ symmetry; thus, the Laue symmetry D_{2h} was indicated. No systematic extinctions were observed for the (hkℓ) reflections; however, the (0kℓ) reflections were observed only when k=2n, the (h0ℓ) reflections occurred only with ℓ=2n and the (hk0) reflections were observed only when h=2n. These characteristic extinctions as well as the observed symmetry indicate the unique space group D_{2h}^{15} - Pbca.

Precision lattice dimensions were determined from data taken with both the standard Weissenberg camera having an effective diameter of 57.291 mm. and a back-reflection Weissenberg camera similar in design to the one described by Buerger (1942, pp. 436-441). The effective diameter of the back-reflection camera used in this investigation was 73.107 mm. The systematic errors inherent in cell constant data diminish as the Bragg angle θ approaches 90°. Thus, extrapolation of such data to θ=90° will result in minimum error. Numerous functions of θ have been derived which produce a linear relationship when certain systematic errors are present in the data. Such a function was proposed by Nelson and Riley (1945) which results in a linear relationship over a large range of values when absorption is the chief source of error. Specimen eccentricity and camera radius errors in the Weissenberg data were considered to be small; thus, the cell dimensions obtained from Weissenberg data were determined by extrapolation against the Nelson-Riley function. The dimension of the unit cell parallel to the rotation axis was determined by extrapolation of rotation data against $\cos^2 \theta$ which produces a linear relationship at large values of θ. The precision lattice dimensions for the orthorhombic unit cell of the zirconium-rich structure were found to be the following:

$$a_o = 12.497 \pm 0.003 \text{ Å}$$
$$b_o = 9.210 \pm 0.005 \text{ Å}$$
$$c_o = 9.325 \pm 0.003 \text{ Å}$$

Since only fourfold and eightfold sets of atomic positions are available for occupancy in the space group D_{2h}^{15} - Pbca both the number of nickel atoms and zirconium atoms must be a multiple of four. A number of stoichiometric ratios of nickel and zirconium were considered and all but $Ni_{10}Zr_7$ were rejected on the basis of composition and density considerations. The range of composition of the phase varies from approximately 45.5 w/o Ni to 48 w/o Ni. The densities of massive alloys through this composition range were determined by water displacement methods and were found to vary from 7.6 to 7.8 g. cm^{-3}. It can be seen from the following list of proposed stoichiometric ratios, that each one is outside either the range of compositions or the range of densities observed for the phase:

$Ni_{36}Zr_{32}$ (41.9 w/o Ni)
$Ni_{40}Zr_{32}$ (44.7 w/o Ni, ρ_c=8.15 g. cm^{-3}.)
$Ni_{36}Zr_{28}$ (45.3 w/o Ni, ρ_c=7.22 g. cm^{-3}.)
$Ni_{44}Zr_{32}$ (47.0 w/o Ni, ρ_c=8.74 g. cm^{-3}.)
$Ni_{36}Zr_{24}$ (49.1 w/o Ni)
$Ni_{44}Zr_{28}$ (50.2 w/o Ni)

Calculations based on observed density data and the above cell dimensions indicate the unit cell content of approximately four formula weights of $Ni_{10}Zr_7$. The maximum zirconium saturation of the phase was established from the previously mentioned phase studies as approximately 45.5 w/o Ni. This composition is equivalent to a cell content of $Ni_{38}Zr_{30}$ or a substitution of two zirconium atoms for nickel atoms in the stoichiometric phase. The theoretical density, based on this zirconium-rich cell content and on the above cell dimensions, was found to be 7.683 g. cm^{-3}. The observed density of a massive alloy of 45.3 w/o Ni composition was measured as 7.67 g. cm.$^{-3}$ which is in good agreement with the assumed cell content.

Requirements of the space group symmetry D_{2h}^{15} - Pbca are such as to allow only special fourfold and general eightfold sets of atomic positions to be occupied. Therefore, the 28 zirconium atoms in the cell will fill one fourfold set and three eightfold sets and the 40 nickel atoms in the cell will occupy five eightfold sets. It should be noted that the stoichiometric cell content was assumed for the purpose of the structure determination, since the effect of the replacement of two nickel atoms by zirconium atoms in the zirconium-rich structure would be small on the calculated structure factors.

Intensity Data

Intensity data for the zirconium-rich sturcture were determined for the $(h0\ell)$ reflections from Weissenberg photographs and for the $(hk0)$ and $(0k\ell)$ reflections from precession photographs. Numerical values of the relative reflection intensities were determined by visual comparison of the diffraction maxima with a set of standard spots of known relative intensity. The ten standard spots were prepared by time exposing a film strip to a given reflection such that the relative values for the spots ranged from 1.0 to 10.0 in intervals of 1.0. The entire range of intensity data for each zone of reflections was obtained from time-exposed photographs. The exposure times for the series of photographs of each zone were varied by a factor of four. In each case, the value of the reflection intensity was estimated from the photographs on which the reflection was first observed. In other words, the value of the reflection intensity was determined from the photograph of lesser exposure on which the reflection first appeared. This procedure is considered to be more accurate than evaluating the intensity on photographs of greater exposure, since at large exposures film blackening is no longer proportional to the exposure. However, the intensity of the corresponding reflection recorded on the film of next greater exposure was estimated as a check if its value fell within the range of the standard intensity spots. If the values for a given reflection did not agree, they were re-evaluated and an average value was determined for that reflection. The relative intensities for reflections which exhibited resolved $K\alpha$ doublets were determined by visual estimation of the relative intensities of the $K\alpha_1$ reflections. This value was then increased by a factor of 3/2 to give a value for the total $K\alpha$ reflection intensity. Values for the relative intensities of 289 independent reflections were determined in this manner.

The intensity data were corrected for Lorentz and polarization effects in a manner depending on the type of data. The precession data were corrected in the manner of Lu (1943) and the Weissenberg data were corrected through the Incor I program of Zalkin and Jones (1956) for the IBM-650 computer. The intensity data were not corrected for absorption errors. The effect of absorption on reflection intensities varies in a manner opposite to that of thermal vibration of the atoms in the crystal. Thus, the two effects tend to oppose one another which reduces the error between observed and calculated structure factors. However, it must be noted that the refined temperature factors become artificial factors and are not a true measure of the amplitude of the thermal oscillations.

Trial Structure

Since only the amplitude and not the phase of the diffracted x-ray beam can be determined experimentally, it becomes necessary to rely on indirect or trial and error methods for the solution of the atomic coordinates of a crystal structure. Numerous attempts have been made to obtain direct solutions of the crystal structure problem. Among these is a method proposed by Harker and Kasper (1948) for centrosymmetric structures which makes use of certain simple inequality relationships between unitary structure factors to establish phase relationships. An attempt was made to apply this method to the structure determination of the zirconium-rich $Ni_{10}Zr_7$ structure. Unitary structure factors were calculated and the inequalities corresponding to the space group symmetry D_{2h}^{15} - Pbca were derived in the manner of Harker and Kasper. However, due to the small magnitudes of the unitary structure factors for this structure, it was not possible to establish the phases of a sufficient number of structure factors to be of value in the structure determination.

Postulation of a trial structure was therefore based on the several Patterson projections: P(x,y), P(x,z), P(y,z) and P(x,y,z). The Patterson function makes use of the square of the structure factor, which is proportional to the integrated reflection intensity, thus eliminating the need of the unknown phase relationships. The resulting Patterson projection is a representation of all interatomic vectors translated to the origin of the cell. The Patterson projections used in this investigation were evaluated through the use of the TDF-2 program of Fitzwater and Williams (1958) for the IBM-650 computer.

Interpretation of the Patterson projections was facilitated by the space group requirement which places a zirconium atom at the origin of the unit cell. Thus, the positions of the numerous peaks on a given Patterson projection will correspond with actual positional parameters for the structure. The Patterson Projection, P(y,z) revealed possible y and z parameters of approximately 4/40, 8/40, 1/4, 12/40 and 16/40. In addition, the projections P(x,y) and P(x,z) suggested similar y and z parameters respectively and indicated possible x parameters of approximately 3/40, 7/40, 1/4, 13/40 and 17/40. The combinations of these trial parameters which resulted in interatomic vectors corresponding to peaks on the Patterson projection and which could be allowed on the basis of spatial considerations, were used to postulate the following trial structure:

space group symmetry: D_{2h}^{15} - Pbca

4 Zr atoms in one fourfold set $(0,0,0;\frac{1}{2},\frac{1}{2},0;0,\frac{1}{2},\frac{1}{2};\frac{1}{2},0,\frac{1}{2})$

24 Zr atoms in three eightfold sets

$\pm(x,y,z;\frac{1}{2}+x,\frac{1}{2}-y,\bar{z};\bar{x},\frac{1}{2}+y,\frac{1}{2}-z;\frac{1}{2}-x,\bar{y},\frac{1}{2}+z)$

40 Ni atoms in five eightfold sets

$\pm(x,y,z;\frac{1}{2}+x,\frac{1}{2}-y,\bar{z};\bar{x},\frac{1}{2}+y,\frac{1}{2}-z;\frac{1}{2}-x,\bar{y},\frac{1}{2}+z)$

The positional parameters for the trial structure are listed in Table 1. In considering spatial requirements, the approximate atomic diameters of $D_{Ni} = 2.4$ Å and $D_{Zr} = 3.1$ Å for metallic bonding were used as guides to ensure that the trial model did not require unreasonable atomic packing.

Preliminary calculations of the structure factors based on these trial parameters revealed good agreement between the calculated and observed structure factors for the $(0k\ell)$ data. Thus, these data indicate that the trial y and z parameters are approximately correct for the structure. With these parameters fixed, new x parameters were chosen on the basis of the Patterson projection $P(x,y,z)$ and spatial requirements.

Table 1. Positional parameters of the first trial structure for the zirconium-rich $Ni_{10}Zr_7$ phase

Atoms	Positions occupied	x/a	y/b	z/c
Zr_0	4(a)	0	0	0
Zr_1	8(c)	13/40	0	0
Zr_2	8(c)	17/40	1/4	1/4
Zr_3	8(c)	27/40	12/40	12/40
Ni_4	8(c)	1/2	0	8/40
Ni_5	8(c)	13/40	0	12/40
Ni_6	8(c)	13/40	12/40	0
Ni_7	8(c)	1/2	8/40	0
Ni_8	8(c)	13/40	4/40	4/40

The resulting parameters of the new trial structure are listed in Table 2.

Refinement of Structure Parameters

The general expression for the structure factor, $F(hk\ell)$, is

$$F(hk\ell) = \sum_{n=1}^{N} f_n \exp 2\pi i(hx_n + ky_n + \ell z_n)$$

This expression can be simplified and the complex quantity eliminated when considering only centrosymmetric structures. The expression can be further simplified when considering only

Table 2. Positional parameters of the second trial structure for the zirconium-rich $Ni_{10}Zr_7$ phase

Atoms	Positions occupied	x/a	y/b	z/c
Zr_0	4(a)	0	0	0
Zr_1	8(c)	13/40	0	0
Zr_2	8(c)	1/4	1/4	1/4
Zr_3	8(c)	1/2	12/40	12/40
Ni_4	8(c)	7/40	0	8/40
Ni_5	8(c)	13/40	0	12/40
Ni_6	8(c)	13/40	12/40	0
Ni_7	8(c)	27/40	8/40	0
Ni_8	8(c)	1/2	4/40	4/40

structures based on the space group symmetry D_{2h}^{15} - Pbca. For structures having this symmetry, the expression for the structure factor becomes:

$$F(hk\ell) = 8 \sum_{n=1}^{N} f_n \cos 2\pi\left(hx_n - \frac{h-k}{4}\right) \cos 2\pi\left(ky_n - \frac{k-\ell}{4}\right) \cos 2\pi\left(\ell z_n - \frac{\ell-h}{4}\right)$$

where h, k and ℓ are the indicies of the reflection, f_n is the atomic scattering factor for the n th atom and x_n, y_n and z_n are the coordinates of the n th atom. The atomic scattering factors used for both nickel and zirconium are those of

Thomas and Umeda (1957). The values of the atomic scattering factors for each observed reflection were evaluated through the Incor I program for the IBM-650 computer.

It has been pointed out earlier that the thermal oscillation of atoms about a given site in a crystal has some effect on the intensity of the diffracted x-ray beam. This effect will tend to reduce the scattering factor of the atom by an amount $\exp(-B_n \sin^2 \theta/\lambda^2)$ where θ is the Bragg angle, λ is the wavelength of the radiation and B_n is a constant known as the temperature factor. Each set of related atoms in a crystal has an individual temperature factor which modifies the scattering factor of these atoms. The thermal motion of the atoms has been treated as isotropic for the purpose of structure factor calculations in this investigation.

Refinement of the trial structure proceeded in three steps. First, the magnitude and phase of the structure factors for each observed reflection were calculated on the basis of the trial structure. The general agreement between the magnitudes of the observed and calculated structure factors justified further refinement of these trial parameters. Two-dimensional Fourier projections were computed with the aid of the TDF-2 computer program from (hk0), (h0ℓ) and (0kℓ) data. The shifts in the positional parameters indicated by these projections were made and a set of approximate positional parameters resulted. These parameters were then refined by the method of least squares using the computer program of Templeton for the IBM-650 as modified by Fitzwater (1958).

The refinement produced a model having calculated structure factors in close agreement with the observed structure factors. The reliability factors, R_1 and R_2, are a measure of the agreement of the calculated and observed structure factors and are defined in the following manner:

$$R_1 = \frac{\Sigma\left||F_o| - |F_c|\right|}{\Sigma\,|F_o|}$$

$$R_2 = \frac{\Sigma(|F_o| - |F_c|)^2}{\Sigma\,F_o^{\,2}}$$

The observed structure factor is F_o and the calculated structure factor is F_c. The value for the reliability factor R_1 for complex structures refined on the basis of visually judged intensity data will range from approximately 0.10 to 0.20 when the proposed model is essentially in agreement with the observed data.

The refined positional parameters along with their standard deviations, given as σ_x, σ_y and σ_z, and temperature factors are listed in Table 3. This model resulted in values for the reliability factors for all data of $R_1 = 0.1631$ and $R_2 = 0.0325$. The reliability factor R_2 was calculated for each zone of reflections and was found to have the following

Table 3. Refined structural parameters for the zirconium-rich $Ni_{10}Zr_7$ phase

No. and kind of atoms	Positions occupied	x/a	y/b	z/c	σ_x	σ_y	σ_z	B_n
4 Zr_0	4(a)	0	0	0	-	-	-	0.575
8 Zr_1	8(c)	0.3356	0.9983	0.9897	0.0008	0.0016	0.0013	1.227
8 Zr_2	8(c)	0.2378	0.2592	0.2440	0.0008	0.0014	0.0013	1.593
8 Zr_3	8(c)	0.4958	0.3156	0.3175	0.0009	0.0013	0.0012	1.280
8 Ni_4	8(c)	0.1950	0.0062	0.2080	0.0012	0.0018	0.0016	0.863
8 Ni_5	8(c)	0.3578	0.0196	0.2964	0.0010	0.0016	0.0014	0.475
8 Ni_6	8(c)	0.3557	0.2941	0.0042	0.0011	0.0017	0.0016	0.701
8 Ni_7	8(c)	0.6406	0.2917	0.0145	0.0010	0.0016	0.0014	0.520
8 Ni_8	8(c)	0.5083	0.1078	0.1023	0.0012	0.0018	0.0017	1.035

values: $R_2(hk0) = 0.0179$, $R_2(h0\ell) = 0.0633$ and $R_2(0k\ell) = 0.0169$. A comparison of the calculated structure factors based on the refined parameters and the observed structure factors is shown in Figure 2. The electron density projections, $\rho(x,y)$ and $\rho(y,z)$, also based on the refined parameters are shown as Figures 3 and 4.

Figure 2. A comparison of observed and calculated structure factors for the refined zirconium-rich $Ni_{10}Zr_7$ structure

hkl	$\lvert F_o \rvert$	F_c
4, 0, 0	5.3	6.60
6, 0, 0	25.3	26.67
8, 0, 0	18.3	18.72
10, 0, 0	3.1	-2.24
12, 0, 0	9.7	10.38
14, 0, 0	11.6	11.40
16, 0, 0	4.5	4.52
18, 0, 0	3.3	-0.92
20, 0, 0	8.7	6.53
22, 0, 0	4.6	4.06
5, 0, 2	3.9	-2.24
6, 0, 2	11.9	13.85
7, 0, 2	<1.3	1.49
8, 0, 2	<1.3	<0.10
9, 0, 2	3.3	6.46
10, 0, 2	7.1	-5.29
11, 0, 2	2.6	0.12
12, 0, 2	3.1	2.57
13, 0, 2	2.6	1.17
14, 0, 2	3.0	3.73
15, 0, 2	2.5	3.88
16, 0, 2	2.6	-3.57
17, 0, 2	<2.2	1.55
18, 0, 2	<2.3	2.40
19, 0, 2	<2.4	1.38
20, 0, 2	<2.2	<0.10
0, 0, 4	24.7	27.02
1, 0, 4	5.4	4.02
2, 0, 4	18.1	-15.57
3, 0, 4	2.0	-4.44
4, 0, 4	6.0	-7.67
5, 0, 4	<1.3	1.40
6, 0, 4	5.5	6.61
7, 0, 4	<1.4	2.57
8, 0, 4	4.3	5.18
9, 0, 4	2.8	-4.56
10, 0, 4	8.3	-10.51
11, 0, 4	<1.8	1.20
12, 0, 4	2.3	3.05
13, 0, 4	<1.9	1.43
14, 0, 4	3.5	3.39
15, 0, 4	<2.1	-2.28
16, 0, 4	<2.2	-0.66
17, 0, 4	<1.4	<0.10
18, 0, 4	5.1	-2.38
19, 0, 4	<1.1	<0.10
20, 0, 4	5.5	2.64
0, 0, 6	12.6	13.07
1, 0, 6	<1.3	1.20
2, 0, 6	2.7	5.70
3, 0, 6	2.5	5.46
4, 0, 6	7.7	-9.73
5, 0, 6	4.7	-7.14
6, 0, 6	17.6	16.81
7, 0, 6	2.6	-0.75
8, 0, 6	2.3	3.07
9, 0, 6	2.7	6.13
10, 0, 6	3.2	-1.29
11, 0, 6	<1.9	-4.13
12, 0, 6	<2.0	2.92
13, 0, 6	<2.1	-2.06
14, 0, 6	6.4	7.07
15, 0, 6	<2.2	2.85
16, 0, 6	<2.3	-0.32
17, 0, 6	<2.4	-0.93
18, 0, 6	<2.5	0.78
19, 0, 6	<2.5	-0.59
20, 0, 6	3.9	2.85
0, 0, 8	7.9	9.06
1, 0, 8	4.6	4.81
2, 0, 8	7.3	-5.67
3, 0, 8	2.3	-2.99
4, 0, 8	2.1	-1.98
5, 0, 8	<1.7	-0.86
6, 0, 8	<1.8	1.11
7, 0, 8	<1.8	1.49
8, 0, 8	2.7	3.78
9, 0, 8	<1.9	-2.49
10, 0, 8	3.5	-6.75
11, 0, 8	<2.1	-0.67
12, 0, 8	3.0	3.53
13, 0, 8	<2.2	0.44
14, 0, 8	<2.3	0.54
15, 0, 8	<2.4	-1.82
16, 0, 8	<2.4	-1.33
17, 0, 8	<2.5	-0.30
18, 0, 8	<2.6	0.66
19, 0, 8	<2.6	-0.61
20, 0, 8	<2.7	0.31
0, 0, 10	14.4	14.64
1, 0, 10	2.3	1.08
2, 0, 10	4.0	4.22
3, 0, 10	3.3	2.52
4, 0, 10	4.1	-3.92
5, 0, 10	4.8	-4.59
6, 0, 10	13.9	14.39
7, 0, 10	3.5	0.83
8, 0, 10	2.6	3.59
9, 0, 10	<2.1	1.79
10, 0, 10	<2.2	1.10
11, 0, 10	<2.3	-2.26
12, 0, 10	<2.3	2.24
13, 0, 10	<2.4	-1.00
14, 0, 10	8.5	7.17
15, 0, 10	<2.5	1.01
16, 0, 10	<2.6	1.36
17, 0, 10	<2.6	-0.96
18, 0, 10	<2.7	-0.79
19, 0, 10	<2.7	-0.30
20, 0, 10	5.3	3.67
0, 0, 12	5.1	5.56
1, 0, 12	4.2	4.23
2, 0, 12	2.6	1.27
3, 0, 12	2.6	0.64
4, 0, 12	4.6	2.50
5, 0, 12	<2.2	-1.87
6, 0, 12	<2.2	2.32
7, 0, 12	<2.3	1.20
8, 0, 12	3.3	4.89
9, 0, 12	<2.3	3.58
10, 9, 12	<2.4	-1.63
11, 0, 12	<2.5	-0.87
12, 0, 12	3.6	4.42
13, 0, 12	<2.6	0.84
14, 0, 12	<2.6	1.50
0, 0, 14	2.9	2.61
1, 0, 14	<2.4	0.96
2, 0, 14	<2.4	-2.45
3, 0, 14	<2.4	0.35
4, 0, 14	5.9	-5.75
5, 0, 14	4.2	-1.60
6, 0, 14	4.3	3.13
7, 0, 14	<2.5	2.04
8, 0, 14	<2.5	-1.68
9, 0, 14	<2.6	-1.10
10, 0, 14	<2.6	-2.10
11, 0, 14	<2.6	0.22
12, 0, 14	<2.6	-1.40
0, 0, 16	4.5	3.89
1, 0, 16	<2.6	2.48
2, 0, 16	<2.6	0.54
3, 0, 16	<2.6	0.94
4, 0, 16	<2.6	0.80
5, 0, 16	2.6	-2.82
6, 0, 16	<2.6	1.95
2, 1, 0	<0.9	-0.94
4, 1, 0	<1.2	1.98
6, 1, 0	<1.4	-3.03
8, 1, 0	4.0	4.05
10, 1, 0	2.6	-3.38
12, 1, 0	3.4	2.46
14, 1, 0	<2.0	-1.51
16, 1, 0	2.7	2.13
2, 2, 0	<1.1	0.55
4, 2, 0	7.3	-6.96
6, 2, 0	11.8	12.26
8, 2, 0	9.5	-11.82
10, 2, 0	7.4	5.67
12, 2, 0	3.9	0.93
14, 2, 0	2.0	-1.30
16, 2, 0	<1.9	-0.40
2, 3, 0	<1.3	2.08
4, 3, 0	2.8	-3.00
6, 3, 0	<1.6	-0.93
8, 3, 0	3.9	-3.63
10, 3, 0	<1.9	2.40
12, 3, 0	5.7	-5.59
14, 3, 0	<2.0	0.28
16, 3, 0	3.1	-2.43
2, 4, 0	15.9	-16.79
4, 4, 0	5.4	-5.46
6, 4, 0	6.7	6.56
8, 4, 0	3.1	2.40
10, 4, 0	8.7	-7.78
12, 4, 0	<2.0	2.72
14, 4, 0	2.8	2.21
16, 4, 0	<1.6	0.16
2, 5, 0	<1.7	0.41
4, 5, 0	<1.7	1.63
6, 5, 0	3.6	-4.33
8, 5, 0	2.6	3.63
10, 5, 0	1.9	-1.61
12, 5, 0	<2.0	0.40
14, 5, 0	<2.0	-1.79
16, 5, 0	2.4	2.36
2, 6, 0	3.1	3.80
4, 6, 0	5.4	-4.76
6, 6, 0	16.8	16.21
8, 6, 0	<2.0	-1.64
10, 6, 0	5.5	3.83
12, 6, 0	<2.0	2.86
14, 6, 0	5.3	4.44
2, 7, 0	2.6	3.35
4, 7, 0	<1.9	-0.27
6, 7, 0	<2.0	0.35
8, 7, 0	<2.0	2.00
10, 7, 0	5.0	5.08
12, 7, 0	<2.0	-2.22
14, 7, 0	4.7	3.89
2, 8, 0	7.8	-7.33
4, 8, 0	3.4	3.13
6, 8, 0	<2.0	1.44
8, 8, 0	<2.0	-1.94
10, 8, 0	<2.0	-0.20
12, 8, 0	<1.8	3.19
2, 9, 0	<2.0	0.98
4, 9, 0	<2.0	0.97
6, 9, 0	4.0	-4.18
8, 9, 0	<2.0	2.41
10, 9, 0	<1.9	-0.11
12, 9, 0	<1.3	-1.20
2, 10, 0	3.4	3.82
4, 10, 0	4.4	-2.86
6, 10, 0	15.7	14.02
8, 10, 0	<1.9	3.28
10, 10, 0	3.2	1.62
2, 11, 0	<1.9	1.51
4, 11, 0	<1.8	-0.90
6, 11, 0	<1.7	-1.82
8, 11, 0	<1.2	0.31
2, 12, 0	3.0	-1.46
4. 12, 0	6.5	5.59
6, 12, 0	2.7	1.07
0, 2, 0	<1.2	1.44
0, 2, 1	<1.2	1.79
0, 2, 2	2.9	5.24
0, 2, 3	5.9	-5.24
0, 2, 4	<1.5	-0.45
0, 2, 5	<1.7	-0.35
0, 2, 6	5.3	4.11
0, 2, 7	7.9	7.06
0, 2, 8	2.6	-3.02
0, 2, 9	<2.2	1.62
0, 2, 10	9.6	8.08
0, 2, 11	<2.2	-0.98
0, 2, 12	4.1	-5.38
0, 4, 0	24.4	26.99
0, 4, 1	12.3	-12.81
0, 4, 2	<1.5	-0.10
0, 4, 3	3.5	2.02
0, 4, 4	27.4	25.03
0, 4, 5	<1.9	-0.61
0, 4, 6	9.9	8.54
0, 4, 7	4.5	-5.33
0, 4, 8	7.6	7.45
0, 4, 9	3.2	1.51
0, 4, 10	6.4	5.76
0, 4, 11	3.0	-3.86
0, 4, 12	2.5	2.48
0, 6, 0	12.3	12.94
0, 6, 1	3.7	3.82
0, 6, 2	4.2	4.55
0, 6, 3	3.2	3.49
0, 6, 4	5.8	7.35
0, 6, 5	<2.1	1.20
0, 6, 6	13.7	14.48
0, 6, 7	<2.2	0.22
0, 6, 8	3.2	-3.28
0, 6, 9	<2.2	2.75
0, 6, 10	9.0	9.28
0, 8, 0	7.7	9.40
0, 8, 1	5.3	-3.77
0, 8, 2	<2.2	-1.01
0, 8, 3	4.4	4.82
0, 8, 4	5.4	7.02
0, 8, 5	2.7	-3.82
0, 8, 6	3.5	-3.70
0, 8, 7	<2.2	-2.86
0, 8, 8	6.1	5.39
0, 8, 9	<1.9	-1.70
0, 8, 10	<1.7	2.61
0, 10, 0	15.2	14.54
0, 10, 1	4.4	-4.71
0, 10, 2	9.7	8.96
0, 10, 3	2.2	0.82
0, 10, 4	5.3	6.31
0, 10, 5	3.3	2.69
0, 10, 6	10.0	9.78
0, 10, 7	3.4	-2.74
0, 10, 8	2.3	3.04
0, 12, 0	3.8	3.62
0, 12, 1	3.2	-3.13
0, 12, 2	3.6	-3.69
0, 12, 3	<2.1	1.02
0, 12, 4	4.0	2.60
0, 12, 5	3.9	-2.54

Figure 3. Fourier projection, $\rho(x,y)$, based on the refined structural parameters of the zirconium-rich $Ni_{10}Zr_7$ phase (the contours are drawn at intervals of 20 arbitrary units)

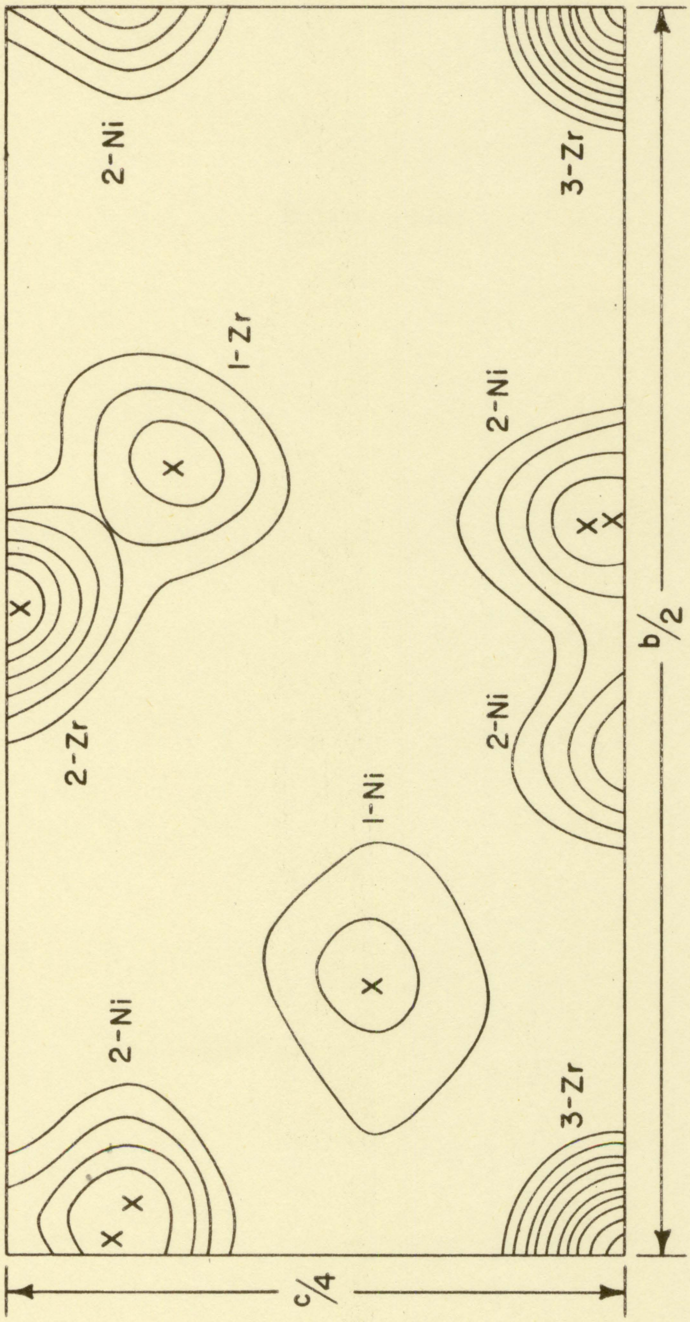
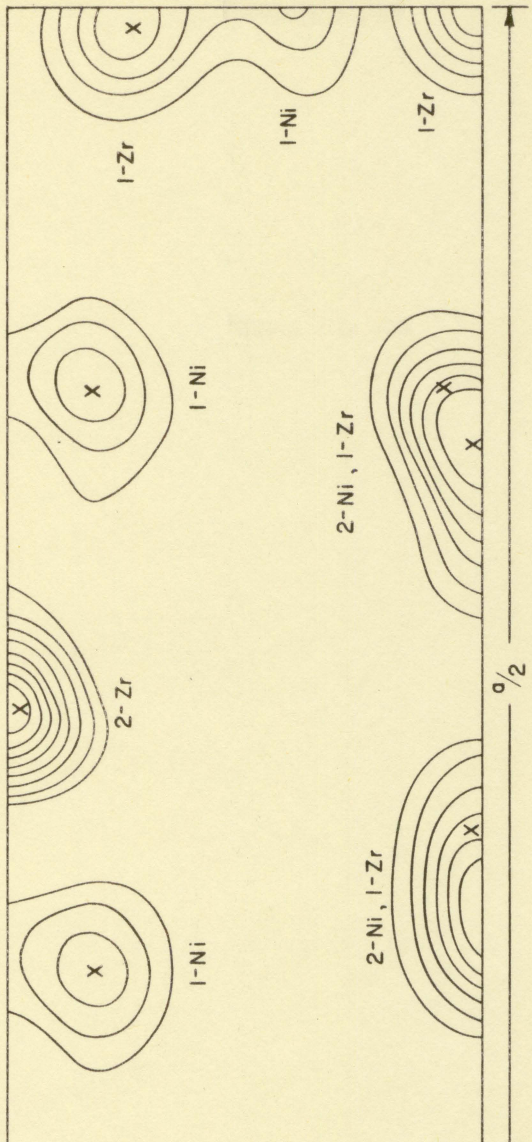

2-Ni
3-Zr
1-Zr
2-Ni
2-Zr
2-Ni
1-Ni
2-Ni
3-Zr
b/2
c/4

Figure 4. Fourier projection, $\rho(y,z)$, based on the refined structural parameters of the zirconium-rich $Ni_{10}Zr_7$ phase (the contours are drawn at intervals of 20 arbitrary units)


1-Zr
1-Ni
1-Zr
1-Ni
2-Ni, 1-Zr
2-Zr
1-Ni
2-Ni, 1-Zr
1-Zr
1-Ni
1-Zr
a/2
b/4

STRUCTURE OF THE STOICHIOMETRIC $Ni_{10}Zr_7$ PHASE

Symmetry and Cell Dimensions

For the purpose of symmetry determination of the stoichiometric $Ni_{10}Zr_7$ structure, $(h0\ell)$ through $(h4\ell)$ Weissenberg and $(0k\ell)$ through $(5k\ell)$ as well as (hk0) through (hk3) precession data were taken. Again, the Laue symmetry D_{2h} was indicated by these data. However, the characteristic extinctions observed for this structure are somewhat different from those observed for the zirconium-rich structure. The general $(hk\ell)$ reflections were observed only with $h + k = 2n$ which indicates a C-centered lattice. The $(0k\ell)$ reflections were observed only with $k = 2n$ which is a redundant condition. The $(h0\ell)$ reflections were observed only when $h + \ell = 2n$. However, a previously established symmetry element requires that $h = 2n$ when $k = 2n$; therefore, the condition $\ell = 2n$ is the only added requirement from the $(h0\ell)$ data and indicates the presence of a (010) glide plane having a translation component c/2. The (hk0) reflections were observed only with $h = 2n$. Again, a previously established symmetry element requires that $h + k = 2n$ which gives rise to the redundant condition $k = 2n$ for the (hk0) reflections. The observed condition that $h = 2n$ for the (hk0) reflections indicates the presence of a (001) glide plane having a translation component a/2. These extinctions indicate the space group symmetry of this structure to be C_{2v}^{17} - C2ca or D_{2h}^{18} - Cmca.

It should be noted at this point that in the interest of uniformity which enables more rapid comparison of the stoichiometric and zirconium-rich structures, the conventional orientation for the noncentrosymmetric space group symmetry was not used. The conventional international symbol for this space group symmetry is C_{2v}^{17} - Aba2. Conversion of this orientation to that used in the text, requires an interchange of the a and c lattice dimensions, h and ℓ reflection indicies and x and z positional parameters.

Precision lattice dimensions for the unit cell of the stoichiometric $Ni_{10}Zr_7$ structure were determined from Weissenberg and rotation data taken with a crystal aligned with the b axis parallel with the axis of rotation. The extrapolation methods used to determine the lattice dimensions were similar to those described for the zirconium-rich $Ni_{10}Zr_7$ structure. The dimensions thus determined are:

$$a_o = 12.386 \pm 0.003 \text{ Å}$$

$$b_o = 9.156 \pm 0.005 \text{ Å}$$

$$c_o = 9.211 \pm 0.004 \text{ Å}$$

On the basis of these cell dimensions and assuming four formula weights of $Ni_{10}Zr_7$ per cell, a theoretical density of 7.791 g. $cm.^{-3}$ was calculated for the structure. This compares with the observed density 7.78 g. $cm.^{-3}$ for a massive alloy of stoichiometric composition. The agreement of these density data as well as space group requirements substantiate the chosen stoichiometry of this phase.

Intensity Data

Intensity data were obtained to establish the space group symmetry and structural parameters for the stoichiometric $Ni_{10}Zr_7$ structure. To record the (h0ℓ) intensity data, Weissenberg timed exposures were taken with Mo Kα radiation. The (0kℓ) intensity data were taken with Mo Kα radiation by timed exposures on a precession camera. The 170 reflection intensities were visually estimated in a manner similar to that described for the zirconium-rich structure.

The similarity of data for this structure with respect to data from the zirconium-rich structure suggests that the stoichiometric structure differs only slightly from that of the refined zirconium-rich structure. Trial structures were postulated which were similar to the refined zirconium-rich structure, but based on the space group symmetries C_{2v}^{17} - C2ca and D_{2h}^{18} - Cmca. Table 4 gives the postulated trial structure based on the centrosymmetric space group D_{2h}^{18} - Cmca. The trial structure based on the noncentrosymmetric space group C_{2v}^{17} - C2ca is given in Table 5.

Since it was impossible to distinguish between the two possible space groups on the basis of symmetry data, it became necessary to determine the true space group symmetry from the observed intensity data. An analytical method developed

Table 4. Positional parameters of a trial structure for the stoichiometric $Ni_{10}Zr_7$ phase based on the space group symmetry D_{2h}^{18} - Cmca

Atoms	Number of Positions	Wyckoff Notation	x/a	y/b	z/c
Zr_0	4	a	0	0	0
Zr_1	8	d	0.33	0	0
Zr_2	8	e	0.25	0.26	0.25
Zr_3	8	f	0	0.32	0.18
$Ni_{4,5}$	16	g	0.20	0.01	0.21
$Ni_{6,7}$	16	g	0.64	0.29	0.01
Ni_8	8	f	0	0.11	0.40

Table 5. Positional parameters of a trial structure for the stoichiometric $Ni_{10}Zr_7$ phase based on the space group symmetry C_{2v}^{17} - C2ca

Atoms	Number of Positions	Wyckoff Notation	x/a	y/b	z/c
Zr_0	4	a	0.05	0	0
Zr_{1a}	4	a	0.38	0	0
Zr_{1b}	4	a	0.71	0	0
Zr_2	8	b	0.29	0.26	0.24
Zr_3	8	b	0.54	0.32	0.32
Ni_4	8	b	0.25	0.01	0.21
Ni_5	8	b	0.41	0.02	0.30
Ni_6	8	b	0.41	0.29	0
Ni_7	8	b	0.69	0.29	0.01
Ni_8	8	b	0.56	0.11	0.10

by Wilson (1949) can be applied under certain circumstances to distinguish between centrosymmetric and noncentrosymmetric crystals. However, since the approximate positional parameters were known for the structure, the determination of the true symmetry was based on the agreement of the amplitudes of the calculated and observed structure factors during the refinement of the proposed trial structures. Since the time required for calculating and comparing structure factors for the centrosymmetric structure is somewhat less than for the noncentrosymmetric structure, the trial model based on the space group symmetry D_{2h}^{18} - Cmca was chosen for the first trial. The attempted refinement of this trial structure was carried out with the aid of the least-squares program for the IBM-650 computer of Templeton as modified by Fitzwater (1958). The reliability factor, R_1 as defined previously, reached the minimum value 0.399 after a number of iteration cycles. A value of this magnitude for R_1 indicates serious error between this trial structure and the actual structure of the stoichiometric $Ni_{10}Zr_7$ phase.

The trial structure based on the space group symmetry C_{2v}^{17} - C2ca was used next for the least-squares refinement. Since a projection of (0kℓ) data for this structure is centrosymmetric, (h0ℓ) data only were used to establish the space group symmetry. Refinement of the x and z positional parameters on the basis of the observed (h0ℓ) intensity data, resulted in x and z positional parameters which gave a reliability factor R_1 of 0.186. A reliability factor in this range is an indication of close agreement between the proposed structure and the actual structure. On the basis of this refinement, the space group symmetry of the stoichiometric $Ni_{10}Zr_7$ structure was established as C_{2v}^{17} - C2ca.

Refinement of Structural Parameters

Examination of the refined x and z positional parameters resulting from the determination of the space group symmetry indicated that the primary difference between the stoichiometric structure and the zirconium-rich structure is that the origin of the cell has been shifted in the x direction creating the noncentrosymmetric symmetry of the stoichiometric $Ni_{10}Zr_7$ structure. Also, it will be noted that the two fourfold sets of atoms, Zr_{1a} and Zr_{1b}, of this trial structure are equivalent to the eightfold set of atoms, Zr_1, in the zirconium-rich structure. During the refinement of this noncentrosymmetric trial structure, these two fourfold sets of atoms were replaced by one eightfold general set. The general y and z parameters of the set refined to zero which makes them equivalent to the fourfold positions. In addition, the refinement produced larger values for R_1 and R_2 with the atoms related in the eightfold positions, thus indicating that the correct positions of these atoms are the two fourfold sets. The refined structure gave the following reliability factors: $R_1 = 0.1661$ and $R_2 = 0.0231$. The final positional parameters along with their standard deviations and temperature factors are listed in Table 6. The calculated and observed structure factors for the refined structure are compared in Figure 5 along with the A and B parts of the calculated structure factors. The electron density projection, $\rho(y,z)$ also based on the refined structural parameters is shown in Figure 6.

Table 6. Refined structural parameters for the stoichiometric $Ni_{10}Zr_7$ phase

No. and kind of atoms	Positions occupied	x/a	y/b	z/c	σ_x	σ_y	σ_z	B_n
4 Zr_0	4(a)	0.0455	0	0	0.0019	-	-	0.816
4 Zr_{1a}	4(a)	0.3566	0	0	0.0014	-	-	0.801
4 Zr_{1b}	4(a)	0.7428	0	0	0.0011	-	-	0.451
8 Zr_2	8(b)	0.2982	0.2560	0.2459	0.0011	0.0012	0.0036	1.158
8 Zr_3	8(b)	0.5471	0.3106	0.3129	0.0016	0.0016	0.0010	1.041
8 Ni_4	8(b)	0.2418	0.0008	0.2100	0.0015	0.0008	0.0008	2.515
8 Ni_5	8(b)	0.4044	0.0082	0.2915	0.0009	0.0019	0.0009	0.503
8 Ni_6	8(b)	0.4022	0.2919	0.0031	0.0010	0.0020	0.0020	0.504
8 Ni_7	8(b)	0.6918	0.2986	0.0122	0.0012	0.0024	0.0014	0.696
8 Ni_8	8(b)	0.5499	0.1090	0.1063	0.0018	0.0021	0.0013	0.699

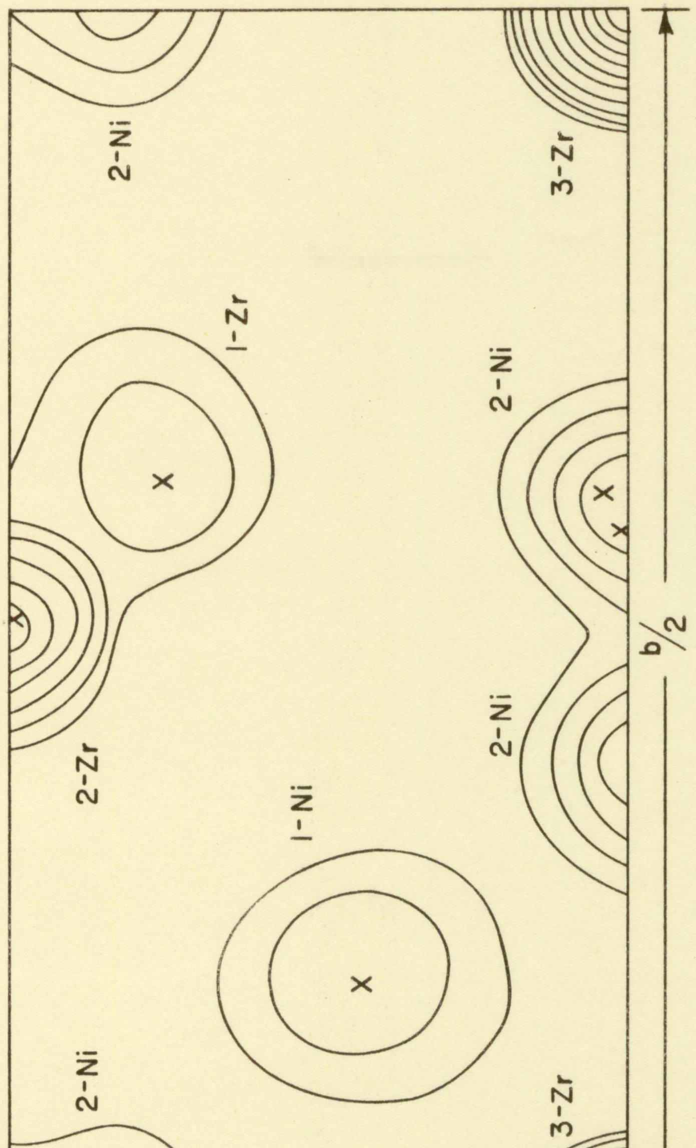
Figure 5. A comparison of observed and calculated structure factors for the refined stoichiometric $Ni_{10}Zr_7$ structure

hk*l*	$\|F_o\|$	$\|F_c\|$	A_c	B_c
800	16.1	17.32	-8.72	14.96
10, 0, 0	2.5	3.76	-3.02	2.24
12, 0, 0	8.1	10.35	-6.18	-8.31
14, 0, 0	12.8	10.67	-7.20	-7.88
16, 0, 0	9.5	9.98	0.03	-9.97
18, 0, 0	5.1	4.85	2.63	4.09
20, 0, 0	13.7	11.23	11.03	-2.16
22, 0, 0	5.3	3.90	3.89	0.25
24, 0, 0	1.5	1.04	0.29	-1.00
26, 0, 0	4.3	3.30	-1.44	2.97
602	11.4	13.13	2.94	12.79
802	7.1	7.10	3.17	-6.35
10, 0, 2	6.2	4.45	-3.86	-2.20
12, 0, 2	4.1	6.38	2.66	5.80
14, 0, 2	3.5	4.92	-1.97	-4.50
16, 0, 2	1.1	2.40	1.51	1.86
18, 0, 2	0.8	1.69	-1.63	0.42
20, 0, 2	0.9	1.43	0.82	-1.17
22, 0, 2	1.7	1.79	1.34	1.19
24, 0, 2	3.2	2.98	-1.84	-2.35
26, 0, 2	2.8	2.40	0.38	2.36
204	17.4	18.07	-14.07	-11.34
404	5.1	3.04	0.06	-3.04
604	4.0	5.34	-3.80	3.76
804	4.5	4.30	0.21	4.29
10, 0, 4	8.6	6.68	6.67	0.28
12, 0, 4	0.8	1.78	0.45	-1.72
14, 0, 4	2.4	2.54	-2.54	-0.01
16, 0, 4	3.0	3.14	-0.49	-3.10
18, 0, 4	7.5	8.38	-5.63	6.20
20, 0, 4	6.5	5.63	5.42	-1.54
22, 0, 4	0.9	1.08	0.16	-1.06
24, 0, 4	2.7	2.93	-0.88	-2.79
26, 0, 4	1.0	0.87	0.64	0.60
28, 0, 4	2.2	1.41	0.06	1.40
206	2.5	3.90	3.58	1.54
406	6.8	6.46	-2.38	-6.00
606	15.6	15.69	-3.57	15.28
806	1.9	2.51	2.50	0.19
10, 0, 6	4.7	5.34	-5.28	0.74
12, 0, 6	2.0	2.40	1.92	1.43
14, 0, 6	8.3	7.76	-4.79	-6.11
16, 0, 6	0.8	0.63	-0.31	-0.55
18, 0, 6	0.8	1.58	-1.37	0.78
20, 0, 6	2.6	3.20	2.89	-1.35
22, 0, 6	4.5	2.84	2.81	0.37
24, 0, 6	3.5	2.93	-1.06	-2.73
26, 0, 6	3.6	2.60	-0.18	2.60
208	8.4	8.60	-7.30	-4.56
408	2.1	0.99	-0.16	0.97
608	0.8	1.25	0.93	0.82
808	0.6	1.74	0.35	0.88
10, 0, 8	2.0	3.34	3.04	-1.39

hk*l*	$\|F_o\|$	$\|F_c\|$	A_c	B_c
12, 0, 8	1.2	1.42	-1.41	0.09
14, 0, 8	2.3	0.65	-0.07	0.65
16, 0, 8	3.1	2.90	1.29	-2.60
18, 0, 8	4.6	4.71	-3.28	3.39
20, 0, 8	3.2	3.74	3.56	-1.16
22, 0, 8	0.9	0.55	-0.54	0.09
24, 0, 8	1.0	1.10	-0.65	-0.88
2, 0, 10	4.2	4.87	4.82	0.66
4, 0, 10	1.9	1.77	-0.76	-1.60
6, 0, 10	14.7	15.71	-6.69	14.21
8, 0, 10	3.1	3.58	0.52	3.54
10, 0, 10	4.3	5.81	-5.59	1.56
12, 0, 10	0.8	2.70	0.84	-2.56
14, 0, 10	10.9	8.96	-5.29	-7.23
16, 0, 10	1.6	2.68	-0.86	-2.54
18, 0, 10	0.9	1.04	0.07	1.04
20, 0, 10	4.2	4.78	4.75	-0.57
22, 0, 10	5.6	3.80	3.77	0.44
2, 0, 12	3.9	3.32	-3.07	-1.26
4, 0, 12	5.1	2.90	0.98	2.73
6, 0, 12	0.8	1.77	1.23	1.27
8, 0, 12	0.8	1.48	-1.38	0.55
10, 0, 12	1.3	0.70	-0.18	0.67
12, 0, 12	3.0	2.19	-2.15	0.38
14, 0, 12	2.2	0.67	-0.24	0.62
16, 0, 12	3.8	2.81	1.14	-2.57
18, 0, 12	1.9	2.26	-1.90	1.22
20, 0, 12	2.7	2.72	2.36	-1.33
2, 0, 14	4.3	3.97	-1.71	-3.58
4, 0, 14	7.7	6.53	-2.64	-5.97
6, 0, 14	5.0	4.48	-3.09	3.24
8, 0, 14	3.6	4.42	4.37	-0.62
10, 0, 14	1.4	1.34	1.13	0.73
12, 0, 14	4.8	4.24	4.24	-0.07
14, 0, 14	3.6	2.32	-1.93	-1.28
16, 0, 14	2.8	1.92	-1.42	1.28
18, 0, 14	4.3	3.45	-1.90	2.88
2, 0, 16	1.4	0.97	-0.64	-0.73
4, 0, 16	4.1	2.56	0.93	2.38
6, 0, 16	1.4	2.37	-0.64	2.28
8, 0, 16	1.5	1.70	-0.80	1.50
10, 0, 16	0.9	1.23	-1.21	0.22
12, 0, 16	2.9	1.67	-1.46	-0.82
14, 0, 16	1.0	1.09	-1.01	-0.40
16, 0, 16	2.3	2.37	0.26	-2.36
2, 0, 18	0.9	0.71	0.43	-0.56
4, 0, 18	1.5	0.98	-0.51	-0.84
6, 0, 18	3.5	3.35	-1.69	2.90
8, 0, 18	1.8	1.30	1.30	0.08
10, 0, 18	2.0	1.57	-1.53	0.34
12, 0, 18	1.5	1.13	0.98	-0.57
2, 0, 20	1.5	1.43	-0.17	-1.43
4, 0, 20	1.0	0.68	-0.09	0.67

hk*l*	$\|F_o\|$	F_c
004	28.4	28.64
006	11.5	12.38
008	11.8	12.29
0, 0, 10	15.8	15.35
0, 0, 12	6.4	7.17
0, 0, 14	3.3	3.44
0, 0, 16	6.3	6.24
0, 0, 18	3.6	2.87
0, 0, 20	5.9	4.29
022	5.6	5.91
023	6.2	-6.30
024	0.2	-0.21
025	0.2	0.17
026	4.8	4.34
027	7.4	6.93
028	0.7	-0.88
029	0.3	-0.51
0, 2, 10	6.2	7.43
0, 2, 11	0.2	-0.87
0, 2, 12	2.5	-3.67
041	11.6	-10.12
042	0.2	-1.27
043	0.3	1.72
044	25.6	26.08
045	0.2	0.45
046	8.4	8.03
047	3.1	-3.62
048	6.7	8.69
049	0.4	2.33
0, 4, 10	5.5	5.48
0, 4, 11	2.0	-2.84
0, 4, 12	4.6	5.46
060	14.1	13.18
061	4.7	6.30
062	5.4	6.04
063	1.6	1.47
064	9.4	8.90
065	0.2	-0.33
066	14.3	14.66
067	0.2	0.40
068	1.6	-1.87
069	0.3	-0.54
0, 6, 10	11.0	10.70
080	11.5	10.34
081	1.0	-1.64
082	0.5	-1.83
083	3.6	3.94
084	6.0	7.34
085	1.1	-2.03
086	3.1	-4.19
087	0.9	-1.82
088	7.1	7.51
0, 10, 0	16.5	16.22
0, 10, 1	2.6	-2.86
0, 10, 2	8.8	8.90
0, 10, 3	0.4	-0.69
0, 10, 4	5.4	6.88
0, 10, 5	0.3	1.66
0, 10, 6	12.6	11.55

Figure 6. Fourier projection, $\rho(y,z)$, based on the refined structural parameters of the stoichiometric $Ni_{10}Zr_7$ phase (the contours are drawn at intervals of 20 arbitrary units)


2-Ni
3-Zr
1-Zr
2-Ni
b/2
2-Zr
2-Ni
1-Ni
2-Ni
3-Zr
c/4

STRUCTURE DETERMINATION OF $Ni_{10}Hf_7$

Symmetry and Cell Dimensions

A single crystal of $Ni_{10}Hf_7$ having a composition equal to that of the nickel-rich phase boundary was used in this investigation. The needle-shaped crystal was orientated in such a manner that the needle axis was parallel to the axis of rotation. Weissenberg and rotation data from a crystal rotated about the b axis were used to establish the lattice dimensions. Extrapolation methods similar to those described for the zirconium-rich phase were employed to determine the following cell dimensions:

$$a_o = 12.275\ \text{Å}$$
$$b_o = 9.078\ \text{Å}$$
$$c_o = 9.126\ \text{Å}$$

Again assuming four formula weights of $Ni_{10}Hf_7$ per unit cell, the theoretical density of the phase based on the observed cell volume was found to be 11.971 g. cm^{-3}. The observed density of a massive alloy of stoichiometric composition was found to be 11.96 g. $cm.^{-3}$ which agrees well with the theoretical density. These data substantiate the assumption of cell content and thus the stoichiometry of the phase.

Symmetry determination of the $Ni_{10}Hf_7$ phase was based on $(h0\ell)$ through $(h4\ell)$ Weissenberg data and $(0k\ell)$ through $(3k\ell)$ as well as (hk0) precession data. All data indicated the Laue symmetry D_{2h}. The characteristic extinctions exhibited by this structure were found to be identical to those for the stoichiometric $Ni_{10}Zr_7$ structure. These extinctions are as follows:

(hkℓ) reflections observed only with h + k = 2n

(0kℓ) reflections observed only with k = 2n*

(h0ℓ) reflections observed only with h = 2n* and ℓ = 2n

(hk0) reflections observed only with k = 2n* and h = 2n

*Redundant conditions

These conditions limit the space group symmetry of the $Ni_{10}Hf_7$ structure to C_{2v}^{17} - C2ca or D_{2h}^{18} - Cmca.

Intensity Data

On the basis of cell dimensions and symmetry data, it was concluded that the stoichiometric $Ni_{10}Hf_7$ phase is isostructural with the stoichiometric $Ni_{10}Zr_7$ phase. However, additional calculations were made to show the correlation between structure factors and relative diffraction intensities. The structure factor calculations were based on the refined structural parameters of the stoichiometric $Ni_{10}Zr_7$ structure. The observed intensity data were obtained from Weissenberg photographs by visual estimation. Numerical values of the relative diffraction intensities were not considered necessary to show the analogy between the $Ni_{10}Zr_7$ and $Ni_{10}Hf_7$ structures. Therefore, the relative intensity values were broken down into six classes which are as follows:

vs - very strong
s - strong
m - medium
w - weak
vw - very weak
no - not observed

A comparison of some of the calculated structure factors, F_c, and the corresponding observed relative intensities is made in Figure 7.

The agreement of these data as well as the similarity of cell dimensions and symmetry data with like data for the stoichiometric $Ni_{10}Zr_7$ structure, were considered adequate evidence to show that the $Ni_{10}Hf_7$ structure is isostructural with the stoichiometric $Ni_{10}Zr_7$ structure. The actual structural parameters for the $Ni_{10}Hf_7$ phase would undoubtedly be slightly different than those of the refined stoichiometric $Ni_{10}Zr_7$ structure due to the small difference in atomic diameters between hafnium and zirconium. For this reason, interatomic distances between neighboring atoms in the $Ni_{10}Hf_7$ structure were not calculated. However, the coordination would be identical with that of the stoichiometric $Ni_{10}Zr_7$ structure.

Figure 7. A comparison of observed intensities and calculated structure factors for the stoichiometric $Ni_{10}Hf_7$ structure

hkℓ	$\lvert F_c \rvert$	Observed Intensity	hkℓ	$\lvert F_c \rvert$	Observed Intensity	hkℓ	$\lvert F_c \rvert$	Observed Intensity
400	28.2	vs	113	14.2	m	028	3.8	vw
600	26.5	vs	313	10.9	s	228	5.7	m
800	17.9	s	513	8.4	w	428	6.2	no
10, 0, 0	5.8	vw	713	6.5	w	628	6.6	m
12, 0, 0	7.2	w	913	5.6	w	828	3.9	no
14, 0, 0	5.7	w	114	5.5	w	0, 2, 10	5.6	w
002	0.8	no	314	16.9	s	2, 2, 10	3.8	w
202	3.5	no	514	3.4	w	4, 2, 10	3.1	vw
402	16.5	m	714	10.0	m	240	21.3	vs
602	16.8	m	914	4.6	w	440	6.6	w
802	12.7	m	115	8.0	w	640	6.0	vw
10, 0, 2	7.7	w	315	9.4	w	840	4.4	vw
12, 0, 2	4.6	w	515	8.1	w	10, 4, 0	1.5	no
14, 0, 2	2.3	no	715	5.2	w	041	14.1	m
004	38.4	vs	116	5.3	w	241	9.1	w
204	21.5	s	316	12.9	m	441	9.8	w
404	4.1	vw	516	1.7	no	641	6.9	w
604	5.5	vw	716	9.7	w	841	6.6	w
804	3.7	vw	117	7.2	w	10, 4, 1	2.9	no
10, 0, 4	1.9	vw	317	4.7	no	042	3.9	vw
12, 0, 4	1.6	vw	517	3.4	no	242	6.7	w
14, 0, 4	1.9	no	118	2.3	w	442	3.0	no
006	15.7	s	318	3.5	no	642	13.7	s
206	5.7	w	518	5.4	no	842	8.7	m
406	2.9	vw	220	2.8	no	10, 4, 2	9.7	m
606	16.5	s	420	8.6	m	043	3.5	no
806	3.4	vw	620	14.4	s	243	1.7	no
10, 0, 6	6.4	m	820	17.6	s	443	2.9	no
12, 0, 6	1.4	no	10, 2, 0	12.0	m	643	0.9	no
008	12.1	m	12, 2, 0	5.3	w	843	1.8	no
208	9.3	m	221	4.9	w	044	29.5	vs
408	1.8	vw	421	6.1	m	244	9.1	m
608	1.5	vw	621	3.1	vw	444	10.1	m
808	1.3	no	821	3.0	vw	644	7.0	w
10, 0, 8	0.6	no	022	25.5	s	844	3.8	vw
0, 0, 10	10.1	m	222	4.6	w	045	1.1	no
2, 0, 10	2.2	vw	422	34.1	vs	245	3.9	no
4, 0, 10	0.3	no	622	3.6	no	445	2.4	no
6, 0, 10	8.2	m	822	2.2	vw	645	2.2	no
8, 0, 10	1.8	no	223	6.4	w	845	0.9	no
111	23.7	s	423	7.4	m	046	9.2	m
311	20.0	s	623	4.0	vw	246	3.3	w
511	16.4	s	823	3.8	w	446	0.9	no
711	12.0	m	024	3.2	no	646	10.8	m
911	8.2	w	224	5.9	m	047	3.4	no
11, 1, 1	5.1	vw	424	1.8	no	247	3.5	no
112	7.8	w	624	12.6	s	447	1.7	no
312	11.1	m	824	10.5	m	647	3.0	no
512	13.4	m	026	10.2	m	847	1.7	no
712	13.4	m	226	11.2	m	048	9.3	m
912	1.2	no	426	10.1	m	248	5.5	w
11, 1, 2	5.6	vw	626	2.9	no	448	3.8	vw

DISCUSSION

The atomic coordination and interatomic distances between neighboring atoms in the unit cell were calculated for both the refined zirconium-rich and stoichiometric structures. These calculations were carried out with the aid of the distance program for the IBM-650 computer. A comparison of these coordinations and interatomic distances for the two structures is made in Table 7. The distances of all atoms within a sphere having a radius of 4.50 Å about the central atom under consideration were calculated. However, only the so-called nearest neighbors were considered in this tabulation. Examination of these distance data revealed a natural cut-off point between nearest-neighbors and second nearest neighbors. The average values for the interatomic distances between the neighboring atoms about a representative atom of each set are compared in Table 8. The average coordination number of zirconium atoms in these structures is 14.29, while the average coordination number of nickel atoms is 10.2. Thus, the average coordination number for the atoms in these structures is 11.90. The average interatomic distances for all Ni-Ni, Zr-Zr, and Ni-Zr bonds in the zirconium-rich and the stoichiometric structures are also shown in Table 8. The atomic diameters given by Pauling (1947) for nickel and zirconium having a coordination number of 12 are 2.488 Å and 3.194 Å respectively. It is of interest to note

Table 7. Interatomic distances in the refined zirconium-rich and stoichiometric structures

		Zr-rich Structure		Stoichiometric Structure			
Atom	Neighbor	No. of Neighbors	Distance, Å	No. of Neighbors			Distance, Å
Zr_0	Zr_3	2	3.37	2			3.36
		2	3.41	2			3.33
	Ni_4	2	3.11	2			3.11
	Ni_5	2	2.61	2			2.60
	Ni_6	2	2.62	2			2.60
	Ni_7	2	2.60	2			2.59
				(Atom-Zr_{1a})		(Atom-Zr_{1b})	
Zr_1	Zr_2	1	3.59	2	3.34	2	3.25
		2	3.42	2	3.32	2	3.38
		1	3.36				
	Zr_3	1	3.24	2	3.40	2	3.44
		1	3.09				
	Ni_4	1	2.69	2	2.40	2	2.67
		1	2.65				
	Ni_5	1	2.88	2	2.75	2	2.77
		1	3.02				
	Ni_6	1	2.74	2	2.73	2	2.74
		1	3.04				
	Ni_7	1	3.11	2	2.75	2	2.81
		1	2.69				
	Ni_8	1	2.60	2	2.77	2	2.77
		1	2.34				

Table 7. (Continued)

		Zr-rich Structure		Stoichiometric Structure	
Atom	Neighbor	No. of Neighbors	Distance, Å	No. of Neighbors	Distance, Å
Zr_2	Zr_1	1	3.59	1	3.34
		2	3.42	1	3.32
		-	-	1	3.25
		1	3.36	1	3.38
	Zr_3	1	3.34	1	3.18
		1	3.12	1	3.20
	Ni_4	1	2.41	1	2.47
		1	2.45	1	2.38
	Ni_5	2	2.72	2	2.67
	Ni_6	1	2.70	1	2.65
		1	2.88	1	2.68
	Ni_7	1	2.74	1	2.76
		1	2.58	1	2.61
Zr_3	Zr_0	1	3.37	1	3.36
		1	3.41	1	3.33
	Zr_1	1	3.24	1	3.40
		1	3.09	1	3.44
	Zr_2	1	3.34	1	3.18
		1	3.12	1	3.20

Table 7. (Continued)

		Zr-rich Structure		Stoichiometric Structure	
Atom	Neighbor	No. of Neighbors	Distance, Å	No. of Neighbors	Distance, Å
Zr_3	Ni_4	1	3.13	1	3.12
	Ni_5	1	3.23	1	3.29
		1	2.83	1	2.71
	Ni_6	1	2.67	1	2.64
	Ni_7	1	2.76	1	2.75
	Ni_8	1	2.79	1	2.83
		1	2.78	1	2.80
		1	2.75	1	2.65
Ni_4	Zr_0	1	3.11	1	3.11
	Zr_1	1	2.69	1	2.40
		1	2.65	1	2.67
	Zr_2	1	2.45	1	2.46
		1	2.41	1	2.37
	Zr_3	1	3.13	1	3.12
	Ni_5	1	2.20	1	2.15
	Ni_6	1	2.80	-	-
	Ni_7	1	2.87	1	2.82
		-	-	1	2.66
	Ni_8	1	3.07	1	3.08
Ni_5	Zr_0	1	2.61	1	2.60
	Zr_1	1	2.88	1	2.75
		1	3.02	1	2.77

Table 7. (Continued)

Atom	Neighbor	Zr-rich Structure No. of Neighbors	Zr-rich Structure Distance, Å	Stoichiometric Structure No. of Neighbors	Stoichiometric Structure Distance Å
Ni_5	Zr_2	1	2.71	1	2.66
		1	2.72	1	2.68
	Zr_3	1	3.23	1	3.29
		1	2.83	1	2.71
	Ni_4	1	2.20	1	2.15
	Ni_6	1	2.59	1	2.63
		-	-	1	2.78
	Ni_7	1	2.74	-	-
	Ni_8	1	2.73	1	2.65
Ni_6	Zr_0	1	2.62	1	2.60
	Zr_1	1	2.74	1	2.73
		1	3.04	1	2.74
	Zr_2	1	2.88	1	2.65
		1	2.70	1	2.68
	Zr_3	1	2.67	1	2.64
	Ni_4	1	2.80	-	-
	Ni_5	1	2.59	1	2.63
		-	-	1	2.78
	Ni_7	1	2.81	1	2.74
	Ni_8	1	2.72	1	2.68
Ni_7	Zr_0	1	2.60	1	2.58

Table 7. (Continued)

Atom	Neighbor	Zr-rich Structure No. of Neighbors	 Distance, Å	Stoichiometric Structure No. of Neighbors	 Distance Å
Ni_7	Zr_1	1	3.11	1	2.81
		1	2.69	1	2.75
	Zr_2	1	2.74	1	2.76
		1	2.58	1	2.62
	Zr_3	1	2.76	1	2.75
	Ni_4	1	2.87	1	2.82
		-	-	1	2.67
	Ni_5	1	2.74	-	-
	Ni_6	1	2.81	1	2.74
	Ni_8	1	2.50	1	2.62
Ni_8	Zr_1	1	2.60	1	2.77
		1	2.34	1	2.77
	Zr_3	1	2.79	1	2.83
		1	2.78	1	2.80
		1	2.75	1	2.65
	Ni_4	1	3.07	1	3.08
	Ni_5	1	2.73	1	2.65
	Ni_6	1	2.72	1	2.68
	Ni_7	1	2.50	1	2.62
	Ni_8	1	2.76	1	2.80

Table 8. Average interatomic distances of nearest neighbors about each atom in the zirconium-rich and stoichiometric $Ni_{10}Zr_7$ structures and the observed change in these distances about nickel atoms

	Coordination			Average interatomic distance, Å Zr-rich structure			Stoichiometric structure			Change of average inter atomic distances %	
Atom	Total	Ni	Zr	Ni-Ni	Zr-Zr	Ni-Zr	Ni-Ni	Zr-Zr	Ni-Zr	Ni-Ni	Zr-Ni
Zr_0	12	8	4	-	3.390	2.735	-	3.345	2.725	-	-
Zr_{1a}	16	10	6	-	3.353	2.776	-	3.353	2.680	-	-
Zr_{1b}	16	10	6	-	3.353	2.776	-	3.357	2.752	-	-
Zr_2	14	8	6	-	3.375	2.650	-	3.278	2.611	-	-
Zr_3	14	8	6	-	3.262	2.868	-	3.318	2.849	-	-
Ni_4	10	4	6	2.735	-	2.740	2.678	-	2.688	2.1	1.9
Ni_5	11	4	7	2.565	-	2.857	2.553	-	2.780	0.5	2.8
Ni_6	10	4	6	2.730	-	2.775	2.708	-	2.673	0.8	3.8
Ni_7	10	4	6	2.730	-	2.747	2.713	-	2.712	0.6	1.3
Ni_8	10	5	5	2.756	-	2.652	2.766	-	2.764	-0.4	-4.1
Average distances				2.706	3.336	2.761	2.688	3.320	2.724		

that the average distances between like atoms in the structures are somewhat larger than the elemental atomic diameters, but the average interatomic distances between unlike atoms is smaller than the sum of the elemental atomic radii. It is apparent from this that the bonding between unlike atoms in this structure is stronger than that between like atoms. A study of the structures of the intermediate phases NiZr and $NiZr_2$ by Kirkpatrick <u>et al.</u> (1960) revealed nickel chains through these structures which would indicate directional nickel-nickel interaction. Examination of the $Ni_{10}Zr_7$ structure did not reveal this directional nickel-nickel bonding.

As can be seen from the comparison of interatomic distances for the zirconium-rich and stoichiometric $Ni_{10}Zr_7$ structures, the coordination and neighboring atom distances about each nickel atom are similar. However, an examination of the change in interatomic distances of atoms about each nickel atom should reveal which nickel atoms are replaced by zirconium atoms in the zirconium-rich structure. The magnitudes of these changes of interatomic distances about each nickel atom are also listed in Table 8 in terms of the per cent change based on the average interatomic distances of the stoichiometric structure. It will be noted that the interatomic distances about the nickel sites Ni_8 in the zirconium-rich structure were observed to be somewhat smaller than those for the stoichiometric structure; thus, indicating that these sites are not probable substitutional sites. The interatomic distances about the remaining nickel sites, Ni_4 through Ni_7, were observed to be expanded in the zirconium-rich structure in comparison with those in the stoichiometric structure. The average interatomic distances between nickel-nickel and nickel-zirconium atoms are comparable; thus the nickel-nickel distances would not be expected to exhibit a significant increase due to zirconium substitution in the structure. However, the difference between the average interatomic distances of nickel-zirconium and zirconium-zirconium atoms is much greater and the effect of zirconium substitutions in nickel sites would be much more apparent from these data. This was indeed found to be the case as can be seen from the data listed in Table 8 concerning the change of interatomic distances about the nickel sites Ni_4 through Ni_7. Calculations based on the assumption that two of the eight nickel sites in any one nickel eightfold set are occupied by zirconium atoms in the zirconium-rich structure indicate that the expansion of nickel-zirconium distances would be approximately 6.0%. The observed expansion of nickel-zirconium distances for any one set of nickel atoms was found to be less than this. However, if the zirconium substitutions for nickel atoms were random in the nickel sites Ni_4 through Ni_7, the expected expansion of nickel-zirconium distances about each of these sites would be approximately 1.5%. This is the same order of magnitude of the changes observed for the nickel-zirconium distances about these nickel sites. These data thus suggest that the probable mechanism of solubility in this intermediate phase is random substitution of zirconium atoms for nickel atoms in the sites Ni_4, Ni_5, Ni_6 and Ni_7.

Calculations based on the deviation of the unit cell volume of the zirconium-rich structure from that of the stoichiometric structure and on the average atomic volumes observed in the stoichiometric structure indicate a change in composition approximately equal to the substitution of two zirconium for nickel atoms. This is equivalent to a solubility range of approximately 3.0 a/o. Metallographic evidence from nickel-zirconium alloys having a composition in this region of the system, clearly indicates the solubility range to be between 2.5 and 3.0 a/o at the maximum limits of the phase.

The theoretical density of the zirconium-rich boundary structure of the $Ni_{10}Zr_7$ phase, based on the cell content $Ni_{38}Zr_{30}$, was found to be 7.683 g. cm.$^{-3}$ which is in good agreement with the observed density of 7.67 g. cm.$^{-3}$ for a massive alloy of 45.3 w/o Ni. Since the calculated solubility range was found to be approximately 3.0 a/o or 2.9 w/o, these data indicate the maximum nickel-rich boundary to be approximately 48 w/o Ni which is near the stoichiometric composition of 47.89 w/o Ni. These data, in turn, further justify the assumption that the composition of the crystals obtained from an alloy rich in nickel (49.5 w/o Ni) as described previously is essentially that of stoichiometry.

The observed space group symmetry changes from C_{2v}^{17} - C2ca to D_{2h}^{15} - Pbca between the stoichiometric composition and that of the zirconium-rich phase boundary. This is actually an increase in symmetry as the composition varies from stoichiometry, although the same number of positional parameters are required to describe both structures. The distortion of the atomic arrangement of the stoichiometric structure by the substitution of zirconium atoms for nickel atoms is presumably responsible for the observed symmetry change. However, this distortion is not great, as can be seen from a comparison of the refined positional parameters for the stoichiometric and zirconium-rich structures. The basic difference between the atomic arrangements of these structures of varied composition is in the restrictions place on the zirconium atoms defined as Zr_1. In the stoichiometric structure, the 8-Zr_1 atoms occupy two unrelated fourfold positions, designated Zr_{1a} and Zr_{1b}. The 8 equivalent zirconium atoms in the zirconium-rich structure occupy one eightfold set of positions which relates these atoms by symmetry. The other major difference between these structures is in the choice of unit cell origin. The origin is shifted slightly in the x direction which produces the change in symmetry from noncentrosymmetric to centrosymmetric.

It should be noted at this point that a symmetry shift with composition such as the one just described could be responsible for a certain amount of confusion and error in phase determinations from polycrystalline x-ray diffraction data. As has been pointed out previously, the diffraction pattern of the zirconium-rich structure exhibits many more reflections than the pattern for the stoichiometric structure due to the difference in symmetry. Thus, the polycrystalline diffraction data for a phase such as this could be misleading and create the impression that a separate phase was responsible for the extra diffraction maxima.

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