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## The Crystal Structure of Hf<sub>8</sub>Ni<sub>21</sub>

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The crystal structure of the intermetallic phase Hf<sub>8</sub>Ni<sub>21</sub> has been determined from single-crystal X-ray diffraction data. Hf<sub>8</sub>Ni<sub>21</sub> crystallizes in space group *P*1̄ with *Z* = 1. The cell parameters are *a* = 6.4275 (12), *b* = 8.0007 (15), *c* = 8.5540 (16) Å, *α* = 75.18 (1), *β* = 68.14 (2) and *γ* = 75.61 (2)°. A conventional *R*(*F*) value of 0.11 was obtained for a full-matrix least-squares refinement, using 1440 independent reflexions. The coordination number for each Hf atom is 15, and for the 11 non-equivalent sets of Ni atoms it varies from 12 to 13. Hf<sub>8</sub>Ni<sub>21</sub> is a high-temperature phase, stable from 1300 ± 20 to 1175 ± 10°C, where it decomposes eutectoidally into Hf<sub>3</sub>Ni<sub>7</sub> and HfNi<sub>3</sub> (low-temperature). The relationship between Hf<sub>8</sub>Ni<sub>21</sub> and Zr<sub>2</sub>Ni<sub>7</sub> is discussed.

### Introduction

Some observations on the Hf–Ni system were reported by Kirkpatrick & Larsen (1961). They stated that a phase of composition Hf<sub>2</sub>Ni<sub>5</sub> existed, and from a comparison of the powder diffraction patterns for Hf<sub>2</sub>Ni<sub>5</sub> and Zr<sub>2</sub>Ni<sub>5</sub> they concluded that the two phases were isostructural. They tentatively indexed Zr<sub>2</sub>Ni<sub>5</sub> on the basis of a pseudo-orthorhombic cell but the symmetry in their Weissenberg photographs appeared to be lower than orthorhombic.

Svechnikov, Shurin & Dmitriyeva (1967) found a phase of composition Hf<sub>2</sub>Ni<sub>5</sub> which formed peritectically from the melt and HfNi<sub>3</sub>, but gave no further characterization of this phase. In an investigation of the Hf–Ni system in the region 65–80 at.% Ni, Bsenko (1978*a*) found that the phase denoted Hf<sub>2</sub>Ni<sub>5</sub> crystallizes with a triclinic unit cell and that the composition is Hf<sub>8</sub>Ni<sub>21</sub>. The investigation of the crystal structure of Hf<sub>8</sub>Ni<sub>21</sub> is presented in this paper.

### Experimental

An alloy of nominal composition Hf<sub>0.28</sub>Ni<sub>0.72</sub> was prepared by arc-melting Hf (containing 3% Zr, Koch-Light) and Ni (Specpure, Johnson Matthey & Co. Ltd)

on a water-cooled Cu hearth. Before the alloy was melted, a getter alloy was melted for five minutes in order to remove oxygen and nitrogen from the protecting Ar atmosphere. The alloy was then placed in a ZrO<sub>2</sub> crucible and heat treated under very pure Ar gas in a resistance furnace for 24 h at 1275°C. This heat treatment is necessary since, when the alloy solidifies in the arc-furnace, the crystals of Hf<sub>8</sub>Ni<sub>21</sub> formed are small and unsuitable for single-crystal X-ray work. During the heat treatment at 1275°C the alloy partly melts and the small crystals of Hf<sub>8</sub>Ni<sub>21</sub> grow larger. After the heat treatment a metallographic examination of the specimen showed large crystals of Hf<sub>8</sub>Ni<sub>21</sub> surrounded by a fine eutectic consisting of Hf<sub>3</sub>Ni<sub>7</sub> and Hf<sub>7</sub>Ni<sub>10</sub>. The sample was then placed in a solution of *aqua regia*, which dissolved the eutectic matrix leaving a batch of Hf<sub>8</sub>Ni<sub>21</sub> crystals. Attempts to obtain crystals of Hf<sub>8</sub>Ni<sub>21</sub> by crushing the sample resulted in severe crystal deformation owing to the great ductility of the phase. A suitable crystal was mounted on a Weissenberg camera and the diffraction symmetry showed the space group to be *P*1̄ or *P*1̄.

A powder diffraction photograph was taken of a sample of small crystals of Hf<sub>8</sub>Ni<sub>21</sub>. A Guinier–Hägg camera (Philips XDC 700) with Cu *K*<sub>α1</sub> radiation (*λ* = 1.54059 Å) was used. Zone-refined Si (*a* = 5.43088 Å) was used as internal standard. The powder pattern was

complex but was successfully indexed on the basis of the cell dimensions obtained from the Weissenberg photographs. The cell parameters were chosen to comply with the conditions for a reduced cell as given in *International Tables for X-ray Crystallography* (1969). The unit-cell dimensions were refined using the local program *CELNE* (Ersson, 1976). The intensity collection was performed in the same way as for the  $\text{HfNi}_3$  phases (Bsenko, 1978*b*). The number of reflexions recorded was 1440 and the  $2\theta$  limit was  $50^\circ$ .

### Refinement of the structure

$F_o^2$  and  $\sigma(F_o^2)$  were obtained after corrections for background, Lorentz and polarization effects had been applied. An absorption correction was calculated ( $\mu = 809 \text{ cm}^{-1}$ ), based on an approximate crystal shape. The crystal was an irregular polyhedron having six boundary planes. The transmission factors varied between 0.02 and 0.25.

The composition of the alloy was first estimated to be  $\text{Hf}_2\text{Ni}_5$  with 28 atoms in the unit cell, but the resulting mean atomic volume calculated from the refined cell volume was too high. A cell content of 29 atoms results in a more probable mean atomic volume and hence the composition was assumed to be  $\text{Hf}_8\text{Ni}_{21}$ .

A three-dimensional Patterson synthesis was computed and the heights and the number of maxima were in accordance with the assumption that the space group was  $P\bar{1}$ . From the largest maxima the positions of the eight Hf atoms in the unit cell were obtained. Based on the positional parameters for the Hf atoms, a Fourier synthesis revealed the positions of 11 non-equivalent Ni atoms. A refinement of the structure was performed using the full-matrix least-squares program *UPALS* (Lundgren, 1976). The function minimized was  $w(|F_o|$

$- |F_c|)^2$ , with weights according to  $w^{-1} = \sigma^2(F_o) - (pF_o)^2$  with  $p = 0.03$ . Atomic scattering factors for Hf and Ni were taken from Cromer & Waber (1965), and dispersion correction factors were from Cromer & Liberman (1970). No extinction correction was made. Refinement of one scale factor, 42 positional parameters and 15 isotropic temperature factors yielded an  $R(F)$  value of 0.11. In view of the strong absorption and the lack of a good geometrical description of the crystal, refinement of anisotropic thermal parameters was not considered worthwhile. The final positional parameters and isotropic temperature factors are given in Table 1.\*

### Discussion of the structure

The pseudo-orthorhombic cell dimensions obtained for  $\text{Zr}_2\text{Ni}_5$  by Kirkpatrick & Larsen (1961) are  $a = 6.5$ ,  $b = 10.1$  and  $c = 12.1 \text{ \AA}$ . The primitive unit cell of  $\text{Hf}_8\text{Ni}_{21}$  can be transformed to a centred triclinic cell by the transformation  $\mathbf{a}' = \mathbf{a}$ ,  $\mathbf{b}' = \mathbf{b} - \mathbf{c}$  and  $\mathbf{c}' = -\mathbf{a} + \mathbf{b} + \mathbf{c}$ , with cell dimensions  $a' = 6.43$ ,  $b' = 10.11$ ,  $c' = 12.12 \text{ \AA}$ ,  $\alpha' = 96.8$ ,  $\beta' = 95.9$  and  $\gamma' = 90.7^\circ$ , which

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33757 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final structural parameters for  $\text{Hf}_8\text{Ni}_{21}$*

E.s.d.'s are in units of the least significant digit. Positional parameters are  $\times 10^4$ , thermal  $\times 10^2$ .

		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ( $\text{\AA}^2$ )
Hf(1)	2(i)	2487 (3)	620 (3)	1072 (3)	16 (5)
Hf(2)	2(i)	688 (3)	4040 (2)	8150 (2)	7 (5)
Hf(3)	2(i)	4312 (3)	4633 (3)	2543 (3)	14 (5)
Hf(4)	2(i)	2452 (3)	9375 (3)	5340 (2)	10 (5)
Ni(1)	2(i)	1191 (10)	529 (8)	8506 (8)	30 (10)
Ni(2)	2(i)	4824 (10)	2052 (8)	7756 (8)	24 (10)
Ni(3)	2(i)	3193 (10)	2416 (8)	5496 (8)	26 (10)
Ni(4)	2(i)	983 (9)	2587 (7)	3474 (7)	16 (10)
Ni(5)	2(i)	2901 (10)	3905 (8)	278 (8)	31 (10)
Ni(6)	2(i)	3164 (10)	5995 (8)	5365 (8)	34 (10)
Ni(7)	2(i)	1354 (10)	7105 (8)	8439 (8)	31 (10)
Ni(8)	2(i)	3048 (10)	7452 (8)	395 (8)	29 (10)
Ni(9)	2(i)	989 (9)	7821 (7)	3448 (7)	18 (10)
Ni(10)	2(i)	4849 (10)	8825 (8)	7436 (8)	35 (10)
Ni(11)	1(g)	0	$\frac{1}{2}$	$\frac{1}{2}$	5 (11)

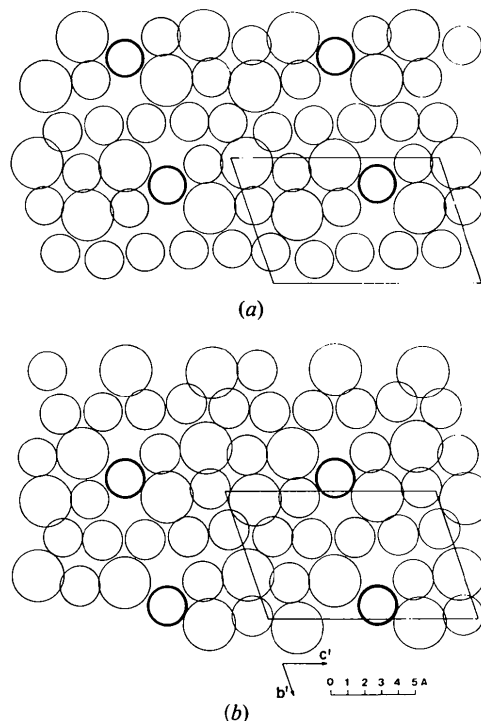


Fig. 1. The two layers of the structure of  $\text{Hf}_8\text{Ni}_{21}$  projected on the (100) plane. The Ni(9) atoms are drawn with a thick line. (a)  $x \sim 0.25$ . (b)  $x \sim 0.75$ .

probably corresponds to the choice of unit cell that Kirkpatrick & Larsen (1961) made for  $\text{Zr}_2\text{Ni}_5$ .

The crystal structure of  $\text{Hf}_8\text{Ni}_{21}$  can be described as a stacking of slightly puckered layers of atoms in a sequence repeated after two layers. The structure is best visualized if a transformation of the unit cell is performed according to  $\mathbf{a}' = \mathbf{a}$ ,  $\mathbf{b}' = \mathbf{b}$  and  $\mathbf{c}' = \mathbf{a} + \mathbf{c}$ .

The corresponding cell dimensions are  $a' = 6.43$ ,  $b' = 8.00$ ,  $c' = 12.46$  Å,  $\alpha' = 72.33$ ,  $\beta' = 39.58$  and  $\gamma' = 75.61^\circ$ . The two layers composing the structure are parallel to the (100) plane and situated at  $x \sim 0.25$  and  $x \sim 0.75$ . Fig. 1 shows the two layers together with the unit-cell contour drawn at  $x = \frac{1}{4}$ . Ni(11) is situated between the two layers. The layers can be regarded as

Table 2. *Interatomic distances (Å) less than 3.5 Å in  $\text{Hf}_8\text{Ni}_{21}$*

E.s.d.'s are in units of the least significant digit.

Hf(1)–Hf(1)	3.117 (3)	Hf(2)–Hf(1)	3.485 (2)	Hf(3)–Hf(2)	3.347 (2)	Hf(4)–Hf(1)	3.498 (2)
Hf(2)	3.485 (2)	Hf(3)	3.347 (2)	Hf(2)	3.430 (2)	Hf(4)	3.282 (3)
Hf(4)	3.498 (2)	Hf(3)	3.430 (2)	Ni(2)	2.773 (5)	Hf(4)	3.461 (3)
Ni(1)	2.611 (5)	Ni(1)	2.704 (5)	Ni(3)	2.651 (5)	Ni(1)	2.844 (5)
Ni(1)	2.647 (5)	Ni(2)	2.687 (5)	Ni(4)	2.775 (5)	Ni(2)	2.912 (5)
Ni(2)	2.632 (5)	Ni(3)	2.680 (5)	Ni(5)	2.605 (5)	Ni(3)	2.637 (5)
Ni(2)	2.764 (5)	Ni(4)	2.850 (5)	Ni(5)	2.657 (6)	Ni(3)	2.729 (5)
Ni(4)	2.653 (5)	Ni(5)	2.600 (6)	Ni(6)	2.680 (6)	Ni(4)	2.757 (5)
Ni(5)	2.595 (6)	Ni(5)	2.665 (6)	Ni(6)	2.718 (5)	Ni(4)	2.803 (5)
Ni(7)	2.639 (5)	Ni(6) × 2	2.676 (6)	Ni(7)	2.708 (5)	Ni(6)	2.624 (5)
Ni(8)	2.652 (5)	Ni(7)	2.731 (6)	Ni(8)	2.683 (5)	Ni(7)	2.757 (6)
Ni(8)	3.274 (5)	Ni(8)	2.679 (5)	Ni(8)	3.089 (5)	Ni(9)	2.792 (5)
Ni(9)	2.714 (5)	Ni(9)	2.861 (5)	Ni(9)	2.956 (5)	Ni(9)	2.831 (5)
Ni(10)	2.657 (6)	Ni(11)	2.776 (2)	Ni(10)	2.679 (6)	Ni(10)	2.664 (6)
Ni(10)	3.426 (6)			Ni(11)	2.785 (2)	Ni(10)	2.673 (6)
Ni(1)–Hf(1)	2.611 (5)	Ni(2)–Hf(1)	2.632 (5)	Ni(3)–Hf(2)	2.680 (5)	Ni(4)–Hf(1)	2.653 (5)
Hf(1)	2.674 (5)	Hf(1)	2.764 (5)	Hf(3)	2.651 (5)	Hf(2)	2.850 (5)
Hf(2)	2.704 (5)	Hf(2)	2.687 (5)	Hf(4)	2.637 (5)	Hf(3)	2.775 (5)
Hf(4)	2.844 (5)	Hf(3)	2.773 (5)	Hf(4)	2.729 (5)	Hf(4)	2.757 (5)
Ni(1)	2.492 (10)	Hf(4)	2.912 (5)	Ni(1)	2.662 (7)	Hf(4)	2.803 (5)
Ni(2)	2.697 (7)	Ni(1)	2.697 (7)	Ni(2)	2.447 (7)	Ni(3)	2.578 (7)
Ni(3)	2.662 (7)	Ni(3)	2.447 (7)	Ni(4)	2.578 (7)	Ni(5)	2.599 (7)
Ni(7)	2.723 (7)	Ni(5)	2.670 (7)	Ni(6)	2.713 (7)	Ni(6)	2.545 (7)
Ni(7)	3.308 (7)	Ni(6)	2.745 (7)	Ni(6)	2.832 (7)	Ni(7)	2.533 (7)
Ni(8)	2.760 (7)	Ni(6)	3.453 (7)	Ni(9)	2.536 (7)	Ni(9)	2.435 (7)
Ni(8)	2.832 (7)	Ni(8)	2.594 (7)	Ni(10)	2.675 (7)	Ni(10)	2.539 (7)
Ni(9)	2.490 (7)	Ni(9)	2.516 (7)	Ni(10)	3.083 (7)	Ni(11)	2.431 (5)
Ni(10)	2.378 (7)	Ni(10)	2.662 (7)	Ni(11)	2.662 (7)		
Ni(5)–Hf(1)	2.595 (6)	Ni(6)–Hf(2)	2.676 (6)	Ni(7)–Hf(1)	2.639 (5)	Ni(8)–Hf(1)	2.652 (5)
Hf(2)	2.600 (6)	Hf(3)	2.680 (6)	Hf(2)	2.676 (6)	Hf(1)	3.274 (5)
Hf(2)	2.665 (6)	Hf(3)	2.718 (5)	Hf(2)	2.731 (6)	Hf(2)	2.679 (5)
Hf(3)	2.605 (6)	Hf(4)	2.624 (5)	Hf(3)	2.708 (5)	Hf(3)	2.683 (5)
Hf(3)	2.657 (6)	Ni(2)	2.745 (7)	Hf(4)	2.757 (6)	Hf(3)	3.089 (5)
Ni(2)	2.670 (7)	Ni(2)	3.453 (7)	Ni(1)	2.723 (7)	Ni(1)	2.760 (7)
Ni(4)	2.599 (7)	Ni(3)	2.713 (7)	Ni(1)	3.308 (7)	Ni(1)	2.832 (7)
Ni(5)	3.399 (10)	Ni(3)	2.832 (7)	Ni(4)	2.533 (7)	Ni(2)	2.594 (7)
Ni(7)	2.781 (7)	Ni(4)	2.545 (7)	Ni(5)	2.781 (7)	Ni(5)	2.468 (7)
Ni(7)	2.805 (8)	Ni(6)	2.460 (10)	Ni(5)	2.805 (8)	Ni(5)	2.891 (7)
Ni(8)	2.468 (7)	Ni(7)	2.729 (8)	Ni(6)	2.729 (8)	Ni(7)	2.413 (7)
Ni(8)	2.891 (7)	Ni(9)	2.498 (7)	Ni(8)	2.413 (7)	Ni(9)	2.506 (7)
Ni(10)	3.006 (8)	Ni(11)	2.504 (5)	Ni(10)	2.678 (7)	Ni(10)	2.447 (8)
Ni(9)–Hf(1)	2.657 (6)	Ni(10)–Hf(1)	2.657 (6)	Ni(11)–Hf(2) × 2	2.776 (2)		
Hf(2)	2.861 (5)	Hf(1)	3.426 (6)	Hf(3) × 2	2.785 (2)		
Hf(3)	2.956 (5)	Hf(3)	2.679 (6)	Ni(3) × 2	2.598 (5)		
Hf(4)	2.792 (5)	Hf(4)	2.664 (6)	Ni(4) × 2	2.431 (5)		
Hf(4)	2.831 (5)	Hf(4)	2.673 (6)	Ni(6) × 2	2.504 (5)		
Ni(1)	2.490 (7)	Ni(1)	2.378 (7)	Ni(9) × 2	2.410 (5)		
Ni(2)	2.516 (7)	Ni(2)	2.662 (7)				
Ni(3)	2.536 (7)	Ni(3)	2.675 (7)				
Ni(4)	2.435 (7)	Ni(3)	3.083 (7)				
Ni(6)	2.498 (7)	Ni(4)	2.539 (7)				
Ni(8)	2.506 (7)	Ni(5)	3.006 (8)				
Ni(11)	2.410 (5)	Ni(7)	2.678 (7)				
		Ni(8)	2.447 (8)				

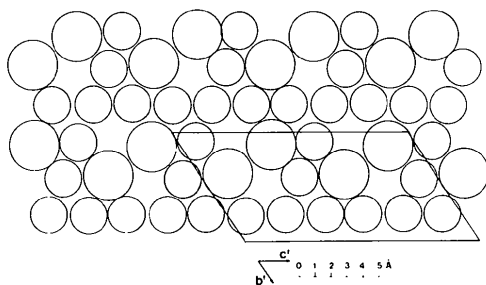


Fig. 2. The layer around  $x \sim 0.25$  of the  $Zr_2Ni_7$  structure projected on the (100) plane.

three rows of atoms parallel to the  $c'$  axis, one row of Ni atoms and two rows of Hf and Ni atoms in a 1:1 ratio. The Ni(9) atoms are situated between the two rows composed of Hf and Ni atoms. When one layer is stacked upon the other, the row of Ni atoms falls between and above the two rows of Hf and Ni atoms. The two rows of Hf and Ni atoms in the upper layer centre the row of Ni atoms in the lower layer.

The relationship between the  $Hf_8Ni_{21}$ -type structure and the structure of  $Zr_2Ni_7$ , determined by Eshelman & Smith (1972) can be visualized if the unit cell of  $Zr_2Ni_7$  is transformed according to  $\mathbf{a}' = -\mathbf{a}$ ,  $\mathbf{b}' = \mathbf{b}$  and  $\mathbf{c}' = \mathbf{b} - \mathbf{c}$ . With this transformation, the structure of  $Zr_2Ni_7$  can be described as a stacking of two layers of atoms at  $x \sim 0.25$  and  $x \sim 0.75$  parallel to the (100) plane. Above and below the layer at  $x \sim 0.25$ , there are four Ni atoms at  $x = 0$  and  $x = \frac{1}{2}$ . The layer at  $x \sim 0.25$  is shown in Fig. 2. The layers at  $x \sim 0.25$  and  $x \sim 0.75$  are closely related to the layers in the  $Hf_8Ni_{21}$ -type structure. There is one straight row of Ni atoms and

two rows of Zr and Ni atoms in a 1:1 ratio parallel to  $c'$ . If the Ni(9) atoms in the  $Hf_8Ni_{21}$ -type structure are shifted and placed in the row of Ni atoms, essentially the same types of layers occur in the two structures.

In the structure of  $Hf_8Ni_{21}$ , the coordination number for the Hf atoms is 15 while the coordination numbers for the Ni atoms vary between 12 and 13. The various interatomic distances less than 3.5 Å are given in Table 2.

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## The Crystal Structure of $Hf_3Ni_7$

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$Hf_3Ni_7$  crystallizes with a new triclinic structure type. The triclinic unit cell, space group  $P\bar{1}$ , contains two formula units and the cell dimensions are  $a = 6.5138$  (11),  $b = 6.5890$  (11),  $c = 7.6271$  (10) Å,  $\alpha = 104.87$  (1),  $\beta = 104.60$  (3) and  $\gamma = 112.71$  (1)°. The structure has been determined and refined from single-crystal three-dimensional X-ray diffraction data. Full-matrix least-squares refinement yielded a conventional  $R(F)$  value of 0.09. The structure can be regarded as a stacking of three slightly puckered layers parallel to the (011) plane.  $Hf_3Ni_7$  is a high-temperature phase, stable from  $1250 \pm 20$  to  $1016 \pm 3$ °C, where it decomposes eutectoidally into  $Hf_7Ni_{10}$  and  $HfNi_3$  (low-temperature).

#### Introduction

In the investigation of the Hf–Ni system in the region 65–80 at.% Ni, Bsenko (1978a) found a phase forming

peritectically from the melt and  $Hf_8Ni_{21}$ . No such phase exists in the Zr–Ni system, which is in agreement with the findings of Kirkpatrick & Larsen (1961). They also made some observations on the Hf–Ni system but