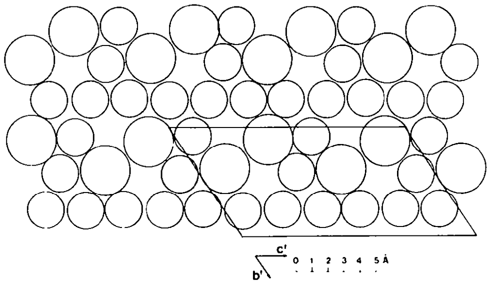

Fig. 2. The layer around $x \sim 0{\cdot}25$ of the Zr_2Ni_7 structure projected on the (100) plane.

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 $x \sim 0{\cdot}25$ and $x \sim 0{\cdot}75$ parallel to the (100) plane. Above and below the layer at $x \sim 0{\cdot}25$, there are four Ni atoms at $x = 0$ and $x = \frac{1}{2}$. The layer at $x \sim 0{\cdot}25$ is shown in Fig. 2. The layers at $x \sim 0{\cdot}25$ and $x \sim 0{\cdot}75$ 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 $\mathbf{c}'$. 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

By Lars Bsenko

Institute of Chemistry, University of Uppsala, Box 531, *S*-751 21 *Uppsala, Sweden*

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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 $a = 6{\cdot}5138\,(11)$, $b = 6{\cdot}5890\,(11)$, $c = 7{\cdot}6271\,(10)$ Å, $\alpha = 104{\cdot}87\,(1)$, $\beta = 104{\cdot}60\,(3)$ and $\gamma = 112{\cdot}71\,(1)°$. 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 ± 20 to 1016 ± 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 (1978*a*) 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 failed to detect this phase. This phase crystallizes in the triclinic system and the ideal composition is Hf_3Ni_7. The purpose of this investigation was to establish the crystal structure of Hf_3Ni_7.

Experimental

By arc-melting Hf (containing 3% Zr, Koch-Light) and Ni (Specpure, Johnson Matthey & Co. Ltd) on a water-cooled Cu hearth, an alloy of nominal composition $Hf_{0\cdot31}Ni_{0\cdot69}$ was prepared. The specimen was then placed in a crucible of ZrO_2 inside a silica tube. The tube was evacuated and sealed off and placed in a resistance furnace at 1200°C for 24 h. At this temperature the phase diagram shows that there is an equilibrium between Hf_3Ni_7 and the melt. After this heat treatment an examination of the polished and etched surface of the sample showed large crystals of Hf_3Ni_7 surrounded by a minor amount of eutectic. Attempts to isolate the crystals by crushing the alloy resulted in severe plastic deformation, and the crystals obtained were unsuitable for single-crystal X-ray work. In order to obtain good crystals the sample was treated with *aqua regia*. The eutectic dissolved in the acid, and crystals of Hf_3Ni_7 were deposited. The crystals were washed in alcohol and dried. A suitable crystal was aligned on a Weissenberg camera and film recordings were made. The symmetry of the reflexions showed that the Hf_3Ni_7 phase crystallizes in the triclinic system with space group $P1$ or $P\bar{1}$. In order to obtain accurate cell dimensions, a powder pattern for a sample of small crystals was recorded in a Guinier–Hägg focusing diffraction camera (Philips XDC 700). Zone-refined Si (a = 5·43088 Å) was used as internal standard and Cu $K\alpha_1$ radiation (λ = 1·54059 Å) was employed. The powder pattern was indexed with the aid of the Weissenberg photographs. The unit-cell parameters were chosen such that the conditions for a reduced cell were fulfilled (*International Tables for X-ray Crystallography*, 1969). The local least-squares program *CELNE* (Ersson, 1976) was used to refine the cell parameters.

The registration of the intensities of Hf_3Ni_7 was performed in the same way as for the $HfNi_3$ phases (Bsenko, 1978*b*). The 2θ limit was 70° and 2360 independent reflexions were recorded.

Refinement of the structure

F_o^2 and $\sigma(F_o^2)$ were obtained from the integrated peak intensities by applying corrections for background, Lorentz and polarization effects, using local programs (Lundgren, 1976). The crystal was of irregular shape and corrections for absorption were calculated for a polyhedron having six boundary planes. The calculated linear absorption coefficient was 834 cm^{-1}. The transmission factors ranged between 0·10 and 0·28.

The composition Hf_3Ni_7 is in good agreement with the observed cell volume if there are two formula units per cell. The positions of the six Hf atoms were obtained from a three-dimensional Patterson synthesis. The heights and the number of the peaks indicated space group $P\bar{1}$. A Fourier synthesis based on these Hf positions revealed the positions of the Ni atoms, and refinement of the structure was started from these preliminary positions.

The full-matrix least-squares program *UPALS* (Lundgren, 1976) was used in the refinement. The function $w(|F_o| - |F_c|)^2$ was minimized with respect to one scale factor, 27 positional parameters and nine isotropic temperature factors. Weights were employed according to the formula $w^{-1} = \sigma^2(F_o) - (pF_o)^2$, where $\sigma^2(F_o)$ was based on counting statistics and the empirical factor p was set at 0·03. No extinction correction was made. The approximate geometrical description of the crystal, together with strong absorption, made a refinement of the anisotropic temperature factors of little significance. Atomic scattering factors and dispersion factors were taken from Cromer & Waber (1965) and Cromer & Liberman (1970) respectively. The final $R(F)$ value based on all reflexions was 0·09. The refined positional parameters and isotropic temperature factors are given in Table 1.*

Discussion of the structure

The structure of Hf_3Ni_7 can be described in terms of a stacking of slightly puckered atomic layers. The transformation $\mathbf{a}' = \mathbf{a}$, $\mathbf{b}' = \mathbf{b}$ and $\mathbf{c}' = \mathbf{b} - \mathbf{c}$ gives a suitable

Table 1. *Final structural parameters for* Hf_3Ni_7

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

		x	y	z	B (Å^2)
Hf(1)	2(*i*)	1568 (1)	250 (1)	3750 (1)	14 (5)
Hf(2)	2(*i*)	983 (1)	4540 (1)	2209 (1)	16 (4)
Hf(3)	2(*i*)	4982 (1)	2720 (1)	1317 (1)	10 (4)
Ni(1)	2(*i*)	4451 (5)	2987 (5)	7346 (4)	22 (8)
Ni(2)	2(*i*)	1825 (5)	3596 (5)	9061 (4)	26 (9)
Ni(3)	2(*i*)	1076 (5)	3856 (5)	5590 (4)	20 (8)
Ni(4)	2(*i*)	2781 (5)	8259 (5)	1076 (4)	22 (8)
Ni(5)	2(*i*)	3820 (5)	8241 (5)	5422 (4)	19 (8)
Ni(6)	2(*i*)	2293 (5)	9360 (5)	7834 (4)	22 (9)
Ni(7)	1(*a*)	0	0	0	15 (8)
Ni(8)	1(*h*)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	13 (8)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33758 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

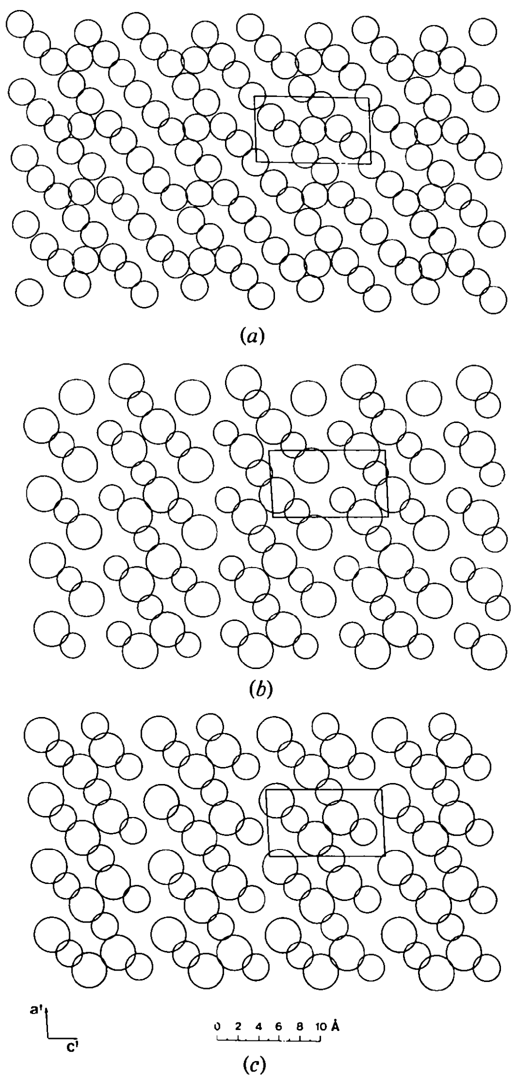

Fig. 1. (*a*) The Ni layer around $y \sim 0$ projected on the (010) plane (unit-cell contour drawn at $y = 0$). (*b*) The Hf and Ni layer around $y \sim 0{\cdot}33$ projected on the (010) plane (unit-cell contour drawn at $y = 0$). (*c*) The Hf and Ni layer around $y \sim 0{\cdot}66$ projected on the (010) plane (unit-cell contour drawn at $y = 0$).

unit cell for the description of the structure. Parallel to the (010) plane of the transformed cell, the stacking of three layers generates the crystal structure. At $y \sim 0$ there is a puckered layer of Ni atoms (Fig. 1*a*), and at $y \sim 0{\cdot}33$ and $y \sim 0{\cdot}66$ there are puckered layers of Hf and Ni atoms in a 1:1 ratio (Fig. 1*b* and *c*). In the Ni layer at $y \sim 0$ the Ni atoms are arranged in parallel rows. One row is fully occupied and the other row consists of one Ni atom and six vacant sites, this arrangement being repeated along the row. The next layer at $y \sim 0{\cdot}33$ can be described as strings of atoms arranged parallel to each other, one string consisting of three Hf and three Ni atoms. This layer is stacked upon the Ni layer in such a way that one string of Hf and Ni atoms fills up the six holes in the Ni layer. The next layer at $y \sim 0{\cdot}66$ is similar to the layer at $y \sim 0{\cdot}33$ but stacked upon this so as to fill the space between the strings. The Ni layer at $y \sim 1{\cdot}0$ is identical to the first layer and is stacked upon the layer at $y \sim 0{\cdot}66$. The six holes in this Ni layer are then filled up with the strings of atoms from the layers below and above.

The coordination numbers for the Hf atoms range from 14 to 15, while those for the Ni atoms range from 12 to 13. Interatomic distances less than 3·5 Å are given in Table 2.

Table 2. *Interatomic distances* (Å) *less than* 3·5 Å *in* Hf_3Ni_7

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

Hf(1)–	Hf(1)	3·105 (2)
	Hf(2)	3·405 (1)
	Hf(3)	3·416 (1)
	Ni(1)	2·624 (3)
	Ni(1)	3·423 (3)
	Ni(2)	2·601 (3)
	Ni(3)	2·653 (3)
	Ni(3)	2·827 (3)
	Ni(4)	2·632 (3)
	Ni(5)	2·616 (3)
	Ni(5)	2·621 (3)
	Ni(6)	2·637 (3)
	Ni(6)	3·249 (3)
	Ni(7)	2·727 (1)
	Ni(8)	2·810 (1)
Hf(2)–	Hf(1)	3·405 (1)
	Hf(3)	3·410 (1)
	Hf(3)	3·444 (1)
	Ni(1)	2·668 (3)
	Ni(2)	2·592 (3)
	Ni(2)	2·677 (3)
	Ni(3)	2·680 (3)
	Ni(3)	2·704 (3)
	Ni(4)	2·654 (3)
	Ni(4)	2·713 (3)
	Ni(5)	2·635 (3)
	Ni(6)	2·618 (3)
	Ni(7)	2·815 (1)
	Ni(8)	2·786 (1)
Hf(3)–	Hf(1)	3·416 (1)
	Hf(2)	3·410 (1)
	Hf(2)	3·444 (1)
	Ni(1)	2·626 (3)
	Ni(1)	3·013 (3)
	Ni(2)	2·650 (3)
	Ni(2)	2·664 (3)
	Ni(3)	2·712 (3)
	Ni(4)	2·665 (3)
	Ni(4)	2·722 (3)
	Ni(5)	2·702 (3)
	Ni(6)	2·658 (3)
	Ni(6)	2·673 (3)
	Ni(7)	2·795 (1)
	Ni(8)	2·870 (1)
Ni(1)–	Hf(1)	2·624 (3)
	Hf(1)	3·423 (3)
	Hf(2)	2·668 (3)
	Hf(3)	2·626 (3)
	Hf(3)	3·013 (3)
	Ni(2)	2·494 (4)
	Ni(2)	2·855 (4)
	Ni(3)	2·604 (4)
	Ni(4)	2·421 (4)
	Ni(5)	2·742 (4)
	Ni(5)	2·960 (4)
	Ni(6)	2·427 (4)
	Ni(8)	2·470 (3)
Ni(2)–	Hf(1)	2·601 (3)
	Hf(2)	2·592 (3)
	Hf(2)	2·677 (3)
	Hf(3)	2·650 (3)
	Hf(3)	2·664 (3)
	Ni(1)	2·494 (4)
	Ni(1)	2·855 (4)
	Ni(3)	2·626 (4)
	Ni(4)	2·731 (4)
	Ni(4)	2·851 (4)
	Ni(6)	2·896 (4)
	Ni(7)	2·559 (3)
Ni(3)–	Hf(1)	2·653 (3)
	Hf(1)	2·827 (3)
	Hf(2)	2·680 (3)
	Hf(2)	2·704 (3)
	Hf(3)	2·712 (3)
	Ni(1)	2·604 (4)
	Ni(2)	2·626 (4)
	Ni(3)	2·579 (5)
	Ni(5)	2·750 (4)
	Ni(5)	2·801 (4)
	Ni(6)	2·679 (4)
	Ni(6)	3·324 (4)
	Ni(8)	2·558 (2)

Table 2 (*cont.*)

Ni(4)–Hf(1)	2·632 (3)	Ni(6)–Hf(1)	2·637 (3)
Hf(2)	2·654 (3)	Hf(1)	3·249 (3)
Hf(2)	2·713 (3)	Hf(2)	2·618 (3)
Hf(3)	2·665 (3)	Hf(3)	2·658 (3)
Hf(3)	2·722 (3)	Hf(3)	2·673 (3)
Ni(1)	2·421 (4)	Ni(1)	2·427 (4)
Ni(2)	2·731 (4)	Ni(2)	2·896 (4)
Ni(2)	2·851 (4)	Ni(3)	2·679 (4)
Ni(5)	2·773 (4)	Ni(3)	3·324 (4)
Ni(5)	3·216 (4)	Ni(4)	2·707 (4)
Ni(6)	2·707 (4)	Ni(4)	2·763 (4)
Ni(6)	2·763 (4)	Ni(5)	2·409 (4)
Ni(7)	2·559 (3)	Ni(7)	2·561 (3)
Ni(5)–Hf(1)	2·616 (3)	Ni(7)–Hf(1) ×2	2·727 (1)
Hf(1)	2·621 (3)	Hf(2) ×2	2·815 (1)
Hf(2)	2·635 (3)	Hf(3) ×2	2·795 (1)
Hf(3)	2·702 (3)	Ni(2) ×2	2·559 (3)
Ni(1)	2·742 (4)	Ni(4) ×2	2·559 (3)
Ni(1)	2·960 (4)	Ni(6) ×2	2·561 (3)
Ni(3)	2·750 (4)		
Ni(3)	2·801 (4)	Ni(8)–Hf(1) ×2	2·810 (1)
Ni(4)	2·773 (4)	Hf(2) ×2	2·786 (1)
Ni(4)	3·216 (4)	Hf(3) ×2	2·870 (1)
Ni(5)	2·563 (5)	Ni(1) ×2	2·470 (3)
Ni(6)	2·409 (4)	Ni(3) ×2	2·558 (2)
Ni(8)	2·517 (3)	Ni(5) ×2	2·517 (3)

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The X-ray Structure of Yeast Inorganic Pyrophosphatase at 5·5 Å Resolution

By Gerard Bunick,* George P. McKenna, F. E. Scarbrough,†
Edward C. Uberbacher and Donald Voet‡

Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104, *USA*

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The structure of yeast inorganic pyrophosphatase has been determined at low resolution (5·5 Å). The phases of the native X-ray intensities are based on the isomorphous replacement and anomalous dispersion data of a single high-quality $Hg(SCN)_4^{2-}$ derivative of the protein. The mean figure of merit for 2214 reflections is 0·817. Crystals of yeast inorganic pyrophosphatase contain one dimeric molecule of molecular weight 64 000 in the asymmetric unit. The overall dimensions of the ellipsoidal molecule, which is clearly distinguishable from the background, are approximately 100 × 50 × 50 Å. The ellipsoid is somewhat indented about its equator with the resulting two lobes of the peanut-shaped dimer being related by an apparent molecular twofold axis.

Introduction

Inorganic pyrophosphatase (EC 3.6.1.1 pyrophosphate phosphohydrolase) catalyzes the hydrolysis of inorganic pyrophosphate to orthophosphate. This reaction disposes of the pyrophosphate ion generated in various biosynthetic reactions thereby driving them to completion (Kornberg, 1962). The failure to find any life forms that lack inorganic pyrophosphatase activity has led to the conclusion that this enzyme is indispensible to living systems (Josse & Wong, 1971).

In higher organisms inorganic pyrophosphatase has been implicated in the formation and maintenance of bones and teeth. The nucleation and growth of hydroxyapatite, a crystalline form of calcium phos-

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* Present address: Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830.

† Present address: HFF-334, Food and Drug Administration, 200 C Street, SW, Washington, DC 20204.

‡ To whom correspondence should be addressed.