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Ternary Rare-earth Transition Metal Phosphides. I. Synthesis and Crystal Structure of $Ho_5Ni_{19}P_{12}$

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Abstract

Single crystals of the new phosphide $Ho_5Ni_{19}P_{12}$ were obtained by reacting the elemental components at high temperature. The compound crystallizes in the hexagonal space-group $P\bar{6}2m$ with the cell constants: $a = 12.288$ (2), $c = 3.762$ (2) Å, $Z = 1$. The structure has been determined from X-ray data and refined to a final R value of 0.049 for 271 independent reflections. It is derivative of the $Hf_2Co_4P_3$-type structure. Holmium atoms are in a trigonal-prismatic phosphorus coordination while nickel atoms occupy three different phosphorus polyhedra: triangle, tetrahedra and 'square-planar' pyramids. The atomic arrangement of $Ho_5Ni_{19}P_{12}$ appears as a combination of those observed in $Zr_2Fe_{12}P_7$ and $Zr_6Ni_{20}P_{13}$-type structures.

Introduction

Our previous work on the Ni–Zr–P system enabled us to synthesize the new compounds $Zr_2Ni_{12}P_7$ and $Zr_6Ni_{20}P_{13}$ with the same metal/non metal ratio [1]. The former is of $Zr_2Fe_{12}P_7$-type [2], the latter is a new structural type in chemistry of ternary transition metal pnictides [3]. In both structures, zirconium atoms occupy trigonal-prismatic phosphorus sites.

The occurrence of ternary compounds $Ln_2Ni_{12}P_7$ [4, 5], isostructural of $Zr_2Ni_{12}P_7$, prompted us to synthesize ternary compounds $Ln_6Ni_{20}P_{13}$ of $Zr_6Ni_{20}P_{13}$-type [3]. During this work, when lanthanoid was holmium, in addition to the expected $Ho_6Ni_{20}P_{13}$ compound, a new compound $Ho_5Ni_{19}P_{12}$ has been obtained at high temperature. The present paper reports the synthesis and structural results for this new compound.

Experimental

Single Crystals Preparation

Samples with the atomic ratio Ho:Ni:P = 6:20:13 were prepared by direct combination of the constituent elements. The starting materials were holmium and nickel powders (minimum purity 99.9%) and red phosphorus (minimum purity 99.99%). The elements were mixed in an argon-filled glove box to prevent oxidation of the rare-earth metal, and placed in alumina crucibles prior to arc-weld sealing inside molybdenum crucibles, under 0.5 atmosphere of argon.

Both alumina and molybdenum crucibles were previously outgassed in a high frequency furnace at 1600 °C under a pressure of 10^{-5} torr. A high-temperature graphite-resistor furnace was used to reach melting temperatures of about 1500 °C, followed by slow cooling at rates of 10–20 °C/h, down to 900 °C. Shiny needle-shaped single-crystals were obtained. Single-crystal investigation performed using the Weissenberg and precession methods (MoKα radiation) pointed out that these crystals were corresponding in fact to two different compounds which both crystallize in the hexagonal symmetry with close unit-cell parameters: $Ho_6Ni_{20}P_{13}$ of $Zr_6Ni_{20}P_{13}$-type ($a = 12.676$ Å, $c = 3.730$ Å) and $Ho_5Ni_{19}P_{12}$ ($a = 12.288$ Å, $c = 3.762$ Å).

Crystal Structure Determination

Single-crystal intensity data of $Ho_5Ni_{19}P_{12}$ were measured on an automatic four circle Nonius diffractometer with graphite-monochromated MoKα radiation. The crystal data and the methods used for intensity collection, structure solution and refinement are summarized in Table I. Unit cell parameters (and orientation matrix) resulted from least-squares refinement of the angular settings of 25 reflections centered on the Nonius diffractometer. The intensities were corrected for Lorentz and polarization effects but not for absorption. The analysis by direct methods and Fourier syntheses were taken from the SDP package implemented on a PDP 11/60 computer [6]. The Laue group is $6/mmm$. In agreement with no systematic extinctions, the possible space groups were $P622$, $P6mm$, $P\bar{6}m2$, $P\bar{6}2m$ and $P6/mmm$. The structure was refined in the non centrosymmetric space group $P\bar{6}2m$.

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TABLE I. Summary of Crystal Data, Intensity Collection and Refinement.

Formula	$Ho_5Ni_{19}P_{12}$
Mol. wt	2311.826
Dimensions (mm)	0.18 × 0.02 × 0.016
Crystal class	hexagonal
a (Å)	12.288 (2)
c (Å)	3.762 (2)
V (Å^3)	492.0 (3)
Z	1
d (calc, g/cm^3)	7.83
space group	$P\bar{6}2m$
Radiation	MoKα = 0.71071 Å
Absorption coefficient (cm^{-1})	389.8
Scan method	$\omega-2\theta$
Data collected	h: −17, +17 k: −17, +17 l: 0, +5
Number of unique reflections	585
Number of reflections $> 2\sigma$	271
Number of observations/number of variables	12
Structure solution	direct methods and Fourier
Refinement	full matrix least squares
Function minimized	$\Sigma\omega(\lvert F_o\rvert - \lvert F_c\rvert)^2$
ω	$1/4\lvert(\sigma(I))^2/I) + p^2I\rvert$ with $p = 0.08$
R	0.049
R_ω	0.057

TABLE II. Positional Parameters and their e.s.d.s.

Atom	Position	x	y	z	B (Å^2)
Ho(1)	3 g	0.8167(2)	0	1/2	0.61 (3)
Ho(2)	2 c	1/3	2/3	0	0.66 (4)
Ni(1)	6 h	0.8720(4)	0.5146(4)	1/2	0.47 (8)
Ni(2)	6 j	0.8152(4)	0.1899(4)	0	0.46 (7)
Ni(3)	3 g	0.2862(6)	0	1/2	0.90 (10)
Ni(4)	3 f	0.4397(5)	0	0	0.26 (9)
Ni(5)	1 a	0	0	0	0.50 (20)
P(1)	6 k	0.5174(8)	0.6859(7)	1/2	0.40 (10)
P(2)	3 f	0.6420(10)	0	0	1.10 (30)
P(3)	3 f	0.1730(10)	0	0	1.10 (20)

In last cycles, secondary extinction coefficient and isotropic temperature factors were included and gave a final R value of 0.049. Anisotropic temperature factors were also tested but did not give significant results. The final positional and thermal parameters are listed in Table II, main interatomic distances in Table III*.

TABLE III. Main Interatomic Distances (Å) and their e.s.d.s.

Ho(1)–2 P(2)	2.847 (12)	Ho(2)–6 P(1)	2.869 (8)
–4 P(3)	2.923 (7)	–6 Ni(1)	3.036 (5)
–2 Ni(5)	2.932 (2)	–3 Ni(2)	3.097 (5)
–4 Ni(2)	3.010 (5)		
–2 Ni(3)	3.074 (6)		
Ni(1)–1 P(1)	2.276 (11)	Ni(2)–1 P(2)	2.245 (9)
–1 P(1)	2.292 (13)	–1 P(3)	2.323 (11)
–2 P(2)	2.450 (7)	–2 P(1)	2.331 (7)
–2 Ni(2)	2.649 (5)	–2 Ni(1)	2.649 (5)
–1 Ni(1)	2.722 (5)	–2 Ni(3)	2.714 (4)
–2 Ni(4)	2.876 (6)	–1 Ni(4)	2.744 (8)
Ni(3)–2 P(1)	2.247 (12)	Ni(4)–1 P(2)	2.487 (17)
–2 P(3)	2.270 (10)	–4 P(1)	2.645 (7)
–2 Ni(4)	2.669 (8)	–2 Ni(3)	2.669 (8)
–4 Ni(2)	2.714 (4)	–2 Ni(2)	2.744 (8)
		–4 Ni(1)	2.876 (6)
		–1 P(3)	3.170 (18)
Ni(5)–3 P(3)	2.227 (17)		
–6 Ho(1)	2.932 (2)		

Crystal Structure

Description

A projection of the crystal structure on the (001) plane is shown in Fig. 1. The structure is characterized by two different holmium atoms which occupy trigonal phosphorus prisms and five different nickel atoms in triangular, tetrahedral or 'square-planar' pyramidal phosphorus coordination.

The structure of $Ho_5Ni_{19}P_{12}$ is derivative of $Hf_2Co_4P_3$-type structure [7]. This latter has the same space group but contains four formula units per cell leading to the formulation $Hf_8Co_{16}P_{12}$.

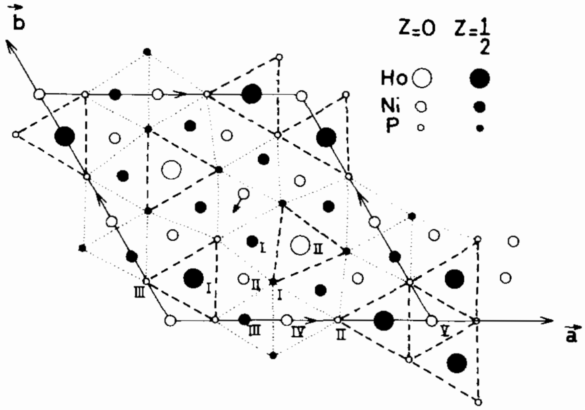

Fig. 1. Projection of the $Ho_5Ni_{19}P_{12}$ structure on the (001) plane. The bold dotted lines indicate the $|HoP_6|$ prisms. Atoms with arrows are in 'square planar' pyramidal phosphorus coordination.

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*Observed and calculated structure factors are available from the authors on request.

In both structures, the number and arrangement of phosphorus polyhedra are the same, *i.e.* fifteen tetrahedra, five trigonal prisms, three 'square-planar' pyramids and one triangle. In $Hf_2Co_4P_3$ structure, pyramids and prisms are occupied by hafnium atoms, tetrahedra and triangle by cobalt atoms. In $Ho_5Ni_{19}P_{12}$ structure, only the prisms are occupied by holmium atoms, the other polyhedra are filled up by nickel atoms. The size of pyramidal sites seems too small for lanthanoid atoms. This result is in accordance with previous studies in lanthanoid pnictides chemistry. The smallest non metal coordination for Ln atoms is either octahedral as found in the monophosphides LnP of rocksalt-type [8, 9] or 6-prismatic as in ternary compounds $Ln_2Ni_{12}P_7$ of $Zr_2Fe_{12}P_7$-type [5].

In the structure, phosphorus atoms occupy tricapped trigonal prism of metal atoms and are all isolated from each other. Thus, no P–P bonds exist contrary to the numerous metal–metal bondings (Table III).

The average Ho–P distance (2.883 Å) is in good agreement with similar distances previously observed in $Ho_2Ni_{12}P_7$ (2.862 Å), $Ho_6Ni_{20}P_{13}$ (2.880 Å) and $Ho_{20}Ni_{66}P_{43}$ (2.870 Å) [10]. The average Ni–P distances vary *vs.* coordination number. The distances in triangular (2.227 Å) and tetrahedral (2.311 Å) coordination are close to those observed in numerous binary and ternary nickel phosphides. However, the average Ni–P distance in pyramidal coordination (2.613 Å), about 6% larger than those previously reported in litterature [3, 11–14], appears probably as a limit value of the Ni–P distance in such a coordination. This may explain why our attempts to synthesize the similar compound $Ho_5Co_{19}P_{12}$ were up to now unsuccessful. Indeed, it is well known that cobalt compounds often have the smallest average atomic volume among the 3d transition compounds [4, 15, 16], even though the atomic volume of elemental Ni is given lower than that of elemental Co [17].

Structural Relationship with Fe_2P, $Zr_2Fe_{12}P_7$, $Zr_6Ni_{20}P_{13}$ and $Hf_2Co_4P_3$-Types

Different structural descriptions have been suggested for numerous binary and ternary pnictides or silicides having a metal/non metal ratio equal or close to two [2, 5, 12, 18–25].

A new way to describe these structures is to consider large triangular units as being built up by metal atoms. One can describe by means of such triangular units the hexagonal structures of Fe_2P (in fact Fe_6P_3) [26], $Zr_2Fe_{12}P_7$ and $Zr_6Ni_{20}P_{13}$. These three structures are the members of a series with general chemical formula $A_{n(n-1)}B_{(n+1)(n+2)}C_{n(n+1)+1}$. Each unit is subdivided into n^2 simple triangular subunits: one subunit in Fe_2P (n = 1), four in $Zr_2Fe_{12}P_7$ (n = 2) and nine in $Zr_6Ni_{20}P_{13}$ (n = 3). Each subunit is occupied either by a phosphorus or a zirconium atom. Fig. 2a, 2b shows the triangular units of $Zr_2Fe_{12}P_7$ (type **I**) and $Zr_6Ni_{20}P_{13}$ (type **II**).

As shown in Fig. 2c, the units of type **I** and type **II** occur in the structure of $Ho_5Ni_{19}P_{12}$. Thus, this structure appears as a combination of the $Zr_2Fe_{12}P_7$ and $Zr_6Ni_{20}P_{13}$-types. In the $Hf_2Co_4P_3$ structure, hafnium atoms, in pyramidal coordination, take part in the construction of type **II** units making them slightly different (Fig. 2d). However, the total framework of both structures is the same.

In conclusion, structural relationship in pnictide chemistry between Fe_2P, $Zr_2Fe_{12}P_7$, $Zr_6Ni_{20}P_{13}$, $Ho_5Ni_{19}P_{12}$ and $Hf_2Co_4P_3$-types is established. In the same way, this relationship can be extended to the binary structures $Rh_{20}Si_{13}$ [18] and $Cr_{12}P_7$ [23] as shown in Scheme 1.

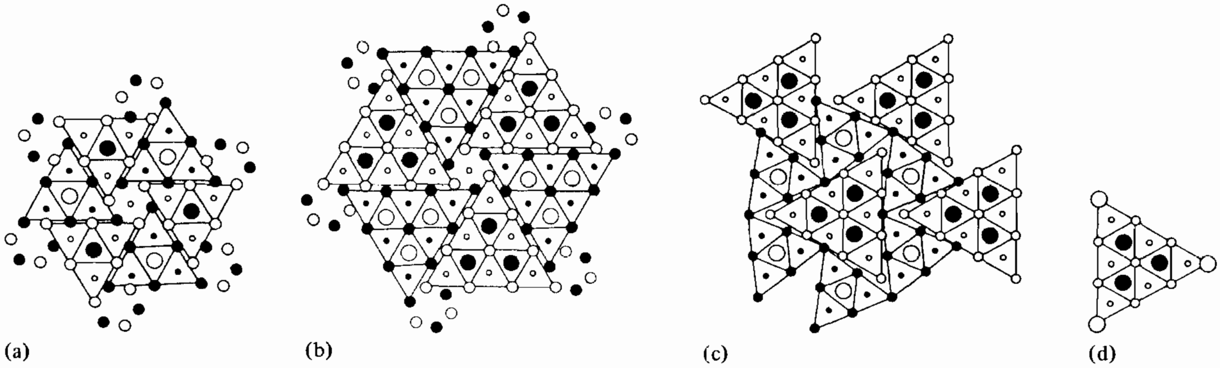
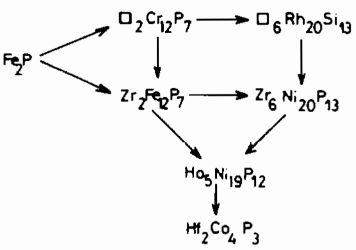


Fig. 2. Schematic representations of: (a) $Zr_2Fe_{12}P_7$; (b) $Zr_6Ni_{20}P_{13}$; (c) $Ho_5Ni_{19}P_{12}$; (d) type **II** unit of $Hf_2Co_4P_3$. Triangular units are emphasized (large circles: Zr, Ho, Hf atoms; medium circles: 3d transition metal atoms; small circles: phosphorus atoms). Black and white circles are translated from each other of half a period of the projection direction.



Scheme 1.

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