Crystal structure of yttrium nickel phosphide, $\text{Y}_{20}\text{Ni}_{42}\text{P}_{30.34}$

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Received July 19th, 2006, accepted and available on-line August 10, 2006; CSD no. 409887

Abstract

$\text{Ni}_{42}\text{P}_{30.34}\text{Y}_{20}$, hexagonal, $P6_3/m$ (no. 176),
 $a = 20.270(1) \text{ \AA}$, $c = 3.8030(2) \text{ \AA}$, $V = 1353.2 \text{ \AA}^3$, $Z = 1$,
 $R_{\text{gt}}(F) = 0.053$, $wR_{\text{ref}}(F^2) = 0.122$, $T = 293 \text{ K}$.

Source of material

A mixture of yttrium ingots, red phosphorous and nickel powders (all with minimum purity 99.95 %) was wrapped in a molybdenum foil, gradually heated to 1070 K in sealed evacuated quartz tube and kept at this temperature for 2 d. Subsequently, the sample was melted in an arc furnace under a Ti-gettered argon atmosphere. Needle-like single crystals of the title compound were extracted from the crushed alloy.

Experimental details

Samples were characterized by X-ray powder diffraction (Huber Image Plate Guinier camera G670, $\text{CuK}\alpha_1$ radiation, $\lambda = 1.54056 \text{ \AA}$, $8^\circ \leq 2\theta \leq 100^\circ$, Ge as internal standard, $a = 5.657905 \text{ \AA}$).

Discussion

The crystal structure of a new ternary phosphide $\text{Y}_{20}\text{Ni}_{42}\text{P}_{31}$ adopts the $\text{Sm}_{20}\text{Ni}_{41.6}\text{P}_{30}$ type [1] and belongs to the homologous family of flat hexagonal two-net structures with a metal/non-metal ratio equal or close to 2 and with the general chemical for-

mula $R_{n(n-1)}T_{(n+1)(n+2)}X_{n(n+1)+1}$ (R - rare earth metal, T - transition metal, X - main group element, $n = 1-6$) [2–4].

For the structural description of $\text{Y}_{20}\text{Ni}_{42}\text{P}_{31}$, one can consider the stacking of trigonal prisms formed by the Y and Ni atoms and centered by P ones. The trigonal prisms, connected only by common edges, are arranged in two identical fragments " $\text{Y}_{10}\text{Ni}_{21}\text{P}_{15}$ " centered on the three-fold axes and mutually displaced by $c/2$ (cf. figure). The coordination number (CN) is 20 for all Y atoms, while for the Ni atoms CN = 9 (Ni3, Ni5 and Ni6), 12 (Ni1, Ni2 and Ni4) and 15 (Ni7 and Ni8). Finally, the P atoms (P1–P5) are in tricapped trigonal prisms (CN = 9), while the P6 one on the six-fold axis occupies the center of a somewhat octahedral site. The shortest interatomic distances observed $d(\text{Ni5}—\text{P1}) = 2.213(7) \text{ \AA}$, $d(\text{Ni2}—\text{Ni7}) = 2.488(6) \text{ \AA}$, $d(\text{Y4}—\text{P5}) = 2.877(5) \text{ \AA}$ and $d(\text{Y4}—\text{Ni5}) = 2.918(3) \text{ \AA}$ are the same order of magnitude than those observed in the crystal structures of all the ternary rare-earth nickel phosphides and the average distances Y—P, Ni—P, Y—Ni and Ni—Ni are in good agreement with the sum of metallic radii of Y (1.77 $\text{ \AA}$) and/or Ni (1.24 $\text{ \AA}$) and the covalent radius of P (1.10 $\text{ \AA}$).

The splitting of the Ni atoms around the sixfold axis in two $6h$ positions partially occupied is due to the splitting of the P6 atom on this axis (one $2b$ position half occupied, since the sites at $z = 0$ and $z = 1/2$ cannot be occupied at the same time. Such a metalloid disorder on 0,0,z coupled to that of the surrounding metal atoms is frequently found in binary or ternary pnictides having hexagonal symmetry and a metal/metalloid ratio equal or close to 2 [5,6].

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Table 1. Data collection and handling.

Crystal:	shiny silvery gray needle, size 0.01 × 0.01 × 0.24 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	361.4 cm ⁻¹
Diffractometer, scan mode:	Nonius KappaCCD, ω
$2\theta_{\max}$:	50.02°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	3209, 934
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 507
$N(\text{param})_{\text{refined}}$:	98
Programs:	SIR97 [7], SHELXL-97 [8], DIAMOND [9]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U_{iso}
Ni(8)	6h	0.18	0.027(1)	0.071(2)	$\frac{3}{4}$	0.021(5)
P(6)	2b	0.17	0	0	$\frac{1}{2}$	0.02(2)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Y(1)	2c		$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$	0.012(2)	U_{11}	0.008(2)	$\frac{1}{2}U_{11}$	0	0
Y(2)	6h		0.1607(1)	0.7020(1)	$\frac{3}{4}$	0.009(1)	0.010(1)	0.011(1)	0.004(1)	0	0
Y(3)	6h		0.3716(1)	0.8756(1)	$\frac{3}{4}$	0.009(2)	0.009(2)	0.010(1)	0.003(1)	0	0
Y(4)	6h		0.1994(1)	0.9093(1)	$\frac{3}{4}$	0.015(2)	0.010(1)	0.010(1)	0.006(1)	0	0
Ni(1)	6h		0.0270(2)	0.6543(2)	$\frac{1}{4}$	0.012(2)	0.011(2)	0.013(2)	0.004(2)	0	0
Ni(2)	6h		0.0665(2)	0.8601(2)	$\frac{1}{4}$	0.008(2)	0.013(2)	0.016(2)	0.003(2)	0	0
Ni(3)	6h		0.4151(2)	0.7936(2)	$\frac{1}{4}$	0.008(2)	0.010(2)	0.012(1)	0.004(2)	0	0
Ni(4)	6h		0.0082(2)	0.5511(2)	$\frac{3}{4}$	0.012(2)	0.011(2)	0.011(2)	0.007(2)	0	0
Ni(5)	6h		0.2433(2)	0.8289(2)	$\frac{1}{4}$	0.007(2)	0.008(2)	0.012(1)	0.004(2)	0	0
Ni(6)	6h		0.0432(2)	0.7566(2)	$\frac{1}{4}$	0.012(2)	0.013(2)	0.014(2)	0.007(2)	0	0
Ni(7)	6h	0.82	-0.0452(2)	0.8798(3)	$\frac{1}{4}$	0.007(2)	0.022(3)	0.022(2)	0.008(2)	0	0
P(1)	6h		0.3254(3)	0.9528(4)	$\frac{1}{4}$	0.012(4)	0.011(4)	0.005(3)	0.007(3)	0	0
P(2)	6h		0.1182(3)	0.7825(4)	$\frac{1}{4}$	0.006(4)	0.008(4)	0.010(3)	0.003(3)	0	0
P(3)	6h		0.2895(4)	0.7478(4)	$\frac{1}{4}$	0.008(4)	0.002(3)	0.008(2)	0.003(3)	0	0
P(4)	6h		0.4958(4)	0.9187(4)	$\frac{1}{4}$	0.008(4)	0.003(3)	0.007(2)	0.000(3)	0	0
P(5)	6h		-0.1688(4)	0.8439(4)	$\frac{1}{4}$	0.015(4)	0.012(4)	0.014(3)	0.008(3)	0	0

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