Letter

Crystal structure of $U_6Ni_{20}P_{13}$ and $U_6Ni_{20}As_{13}$

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1. Introduction

The rare earth–transition metal pnictides have been the subject of extensive studies over the past years. Interest in these compounds has stemmed from their structural chemistry and their interesting magnetic and transport properties. Similar studies but involving uranium and the transition metals, especially copper, nickel and ·palladium, have been carried out in recent years in our laboratories. This paper describes the preparation and single-crystal X-ray structure determination of the new ternary uranium nickel phosphide and arsenide with the compositions $U_6Ni_{20}P_{13}$ and $U_6Ni_{20}As_{13}$.

2. Experimental details

Single crystals of $U_6Ni_{20}P_{13}$ and $U_6Ni_{20}As_{13}$ were obtained by heating powders with the initial compositions UNi_4P_2 or UNi_4As_2 in sealed molybdenum crucibles, at a temperature of about 1500 °C for 2 h and subsequent slow cooling. For this purpose we used a high temperature carbon resistor furnace. From the obtained bulk materials, small single crystals were isolated.

3. Crystallographic study

Diffraction studies were performed on an automatic Enraf–Nonius CAD4 four-circle diffractometer with Mo Kα radiation ($\lambda = 0.71069$ Å). The lattice parameters were calculated by a least-squares technique applied to the setting angles of 25 reflections. Crystallographic data and other important parameters are summarized in Table 1.

TABLE 1

Summary of crystallographic data

Formula	$U_6Ni_{20}P_{13}$	$U_6Ni_{20}As_{13}$
Crystal system	Hexagonal	Hexagonal
Space group	$P6_3/m$	$P6_3/m$
Lattice parameters (Å)		
a	12.664(4)	13.044(4)
b	12.664(4)	13.044(4)
c	3.789(2)	3.888(2)
Volume ($Å^3$)	526.3	572.9
Z	1	1
Calculated density (g cm^{-3})	9.48	10.36
Radiation	Graphite-monochromated Mo $K\alpha$	
μ (Mo $K\alpha$) (cm^{-1})	620	747
Scan mode	$\omega–2\theta$	$\omega–2\theta$
2θ range	0–70	0–70
Number of unique data	954	1039
Number of unique data ($I > 3\sigma(I)$)	426	591
$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$	0.039	0.035
$R_w = (\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2))^{1/2}$	0.046	0.036
$\omega = 1/\sigma(F^2)$		

TABLE 2

Positional parameters and their estimated standard deviations for $U_6Ni_{20}P_{13}$

Atom	Position	x	y	z	B ($Å^2$)	Occupancy
U	6h	0.53133(6)	0.81260(6)	$\frac{1}{4}$	0.58(1)	1
Ni(1)	6h	0.7550(2)	0.0744(2)	$\frac{1}{4}$	0.92(5)	1
Ni(2)	6h	0.4135(2)	0.9765(3)	$\frac{1}{4}$	0.86(5)	1
Ni(3)	2d	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{4}$	0.94(7)	1
Ni(4)	6h	0.0895(4)	0.8971(4)	$\frac{1}{4}$	1.20(9)	0.52
Ni(5)	6h	0.9321(7)	0.0793(7)	$\frac{3}{4}$	2.2(1)	0.46
P(1)	6h	0.6120(5)	0.1360(5)	$\frac{1}{4}$	0.65(9)	1
P(2)	6h	0.9535(5)	0.2322(5)	$\frac{1}{4}$	0.8(1)	1
P(3)	2a			$\frac{3}{4}$	3.7(8)	0.42

Systematic absence of the reflections of the type 000l, $l = 2n + 1$, indicate the hexagonal space group $P6_3/m$ or $P6_3$ (but it eliminates the space group $P\bar{6}$). A survey of the literature suggested these crystals to have the same formula and to be isostructural with a series of other ternary rare earth, zirconium and uranium pnictides [1–3]. In fact representatives of the two latter groups of compounds, i.e. $Zr_6Ni_{20}P_{13}$ and $U_6Rh_{20}P_{13}$, have previously been described in lower Laue symmetry (space group, $P\bar{6}$) [1, 2], but atoms can be associated in pairs, with highly correlated positions ($1 - x$, $1 - y$, $1 - z$), and $Ho_6Ni_{20}P_{13}$ has further been described in $P\bar{6}_3/m$ [3].

The intensities were corrected for Lorentz and polarization effects and a spherical-type absorption correction was applied. Subsequently, the data

TABLE 3

Positional parameters and their estimated standard deviations for $U_6Ni_{20}As_{19}$

Atom	Position	x	y	z	B (Å^2)	Occupancy
U	6h	0.53173(4)	0.81198(5)	$\frac{1}{4}$	0.616(8)	1
Ni(1)	6h	0.7530(2)	0.0727(2)	$\frac{1}{4}$	0.94(4)	1
Ni(2)	6h	0.4123(2)	0.9769(2)	$\frac{1}{4}$	0.92(4)	1
Ni(3)	2d	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0.97(5)	1
Ni(4)	6h	0.0866(4)	0.8902(4)	$\frac{1}{4}$	1.31(8)	0.54
Ni(5)	6h	0.9376(5)	0.0800(5)	$\frac{3}{4}$	1.7(1)	0.42
As(1)	6h	0.6119(1)	0.1365(1)	$\frac{1}{4}$	0.79(3)	1
As(2)	6h	0.9532(1)	0.2298(1)	$\frac{1}{4}$	0.84(3)	1
As(3)	2a			$\frac{3}{4}$	2.0(2)	0.36

were corrected for absorption by means of the DIFABS program [4]. All calculations were carried out on a microVAX 3100 computer with the use of SDP crystallographic software [5]. The positions of all atoms were assigned by analogy with a previously reported structure [3]. Refinement was performed by a full matrix least-squares calculation that included a site population analysis. The final values of the discrepancy factor R were 0.039 and 0.035 for $U_6Ni_{20}P_{13}$ and $U_6Ni_{20}As_{13}$ respectively. Refinements including anisotropic thermal parameters were not significant. The final positional and thermal parameters are listed in Tables 2 and 3. Selected interatomic distances are gathered in Table 4.

4. Description of the structure

The detailed description of the structure under consideration has already been reported [3] in the case of $Ho_6Ni_{20}P_{13}$. In this type of structure the pnictogen (Pn) atoms form various types of arrangement, such as tetrahedra (Tet), pyramids (Pyr), trigonal prisms (Pri) and triangles (Tr). The trigonal prism edges are situated along the c axis.

The uranium atom occupies two groups of three trigonal prisms of pnictogen atoms in the unit cell. In each group, the trigonal prisms are linked together by common edges, yielding in this way the two triangular pnictogen atom sites, each occupied by the Ni(3) atom. The interprism U–U distances in such a group are 3.899 Å and 4.019 Å, while the U–Ni(3) distances are 2.943 Å and 3.027 Å for the phosphide and arsenide respectively. The latter are the shortest distances in comparison with the other U–Ni distances in the unit cell. On the contrary, the shortest U–U distances are those along the c axis and their values are equal to the lattice parameter c. The above two groups of trigonal prisms are separated from each other by two $Ni(1)Pn_4$ and two $Ni(2)Pn_4$ tetrahedra, connected alternatively by their edges. Of the remaining nickel atoms in the unit cell, Ni(4) are placed

TABLE 4

Interatomic distances in $U_6Ni_{20}P_{13}$ and $U_6Ni_{20}As_{13}$

$U_6Ni_{20}P_{13}$		$U_6Ni_{20}As_{13}$	
Atoms	Distance (Å)	Atoms	Distance (Å)
U–2P(2)	2.875(5)	U–2As(2)	2.969(1)
U–2P(1)	2.914(5)	U–2As(1)	3.001(1)
U–2P(1)	2.959(5)	U–2As(1)	3.035(1)
U–2Ni(3)	2.943(1)	U–2Ni(3)	3.027(1)
U–2Ni(1)	3.012(3)	U–2Ni(1)	3.102(1)
U–2Ni(2)	3.057(3)	U–2Ni(2)	3.144(2)
U–1Ni(4)	3.073(9)	U–1Ni(4)	3.104(8)
U–1Ni(2)	3.083(3)	U–1Ni(2)	3.162(1)
U–1Ni(1)	3.102(3)	U–1Ni(1)	3.175(1)
U–1Ni(2)	3.104(3)	U–1Ni(2)	3.226(1)
Ni(1)–1P(2)	2.300(7)	Ni(1)–1As(2)	2.380(1)
Ni(1)–1P(1)	2.301(8)	Ni(1)–1As(1)	2.369(2)
Ni(1)–2P(2)	2.338(4)	Ni(1)–2As(2)	2.399(1)
Ni(1)–1Ni(4)	2.477(5)	Ni(1)–1Ni(4)	2.475(6)
Ni(1)–2Ni(4)	2.625(5)	Ni(1)–2Ni(4)	2.716(7)
Ni(1)–1Ni(5)	2.649(9)	Ni(1)–1Ni(5)	2.715(6)
Ni(1)–2Ni(2)	2.680(8)	Ni(1)–2Ni(2)	2.730(1)
Ni(1)–2U	3.012(3)	Ni(1)–2U	3.102(1)
Ni(1)–1U	3.102(3)	Ni(1)–1U	3.175(1)
Ni(2)–1P(2)	2.283(4)	Ni(2)–1As(2)	2.362(4)
Ni(2)–2P(1)	2.294(4)	Ni(2)–2As(1)	2.366(1)
Ni(2)–1P(1)	2.307(7)	Ni(2)–1As(1)	2.386(2)
Ni(2)–2Ni(1)	2.680(8)	Ni(2)–2Ni(1)	2.730(1)
Ni(2)–2Ni(2)	2.728(2)	Ni(2)–2Ni(2)	2.828(1)
Ni(2)–2U	3.057(3)	Ni(2)–2U	3.144(2)
Ni(2)–1U	3.083(3)	Ni(2)–1U	3.162(1)
Ni(2)–1U	3.104(3)	Ni(2)–1U	3.226(1)
Ni(3)–3P(1)	2.235(6)	Ni(3)–2As(1)	2.296(1)
Ni(3)–6U	2.943(1)	Ni(3)–6U	3.027(1)
Ni(4)–1P(3)	2.112(9)	Ni(4)–1As(3)	2.224(8)
Ni(4)–1P(2)	2.189(7)	Ni(4)–1As(2)	2.292(3)
Ni(4)–2P(2)	2.383(8)	Ni(4)–2As(2)	2.384(3)
Ni(4)–1Ni(5)	0.496(9)	Ni(4)–1Ni(5)	0.612(9)
Ni(4)–1Ni(1)	2.477(5)	Ni(4)–1Ni(1)	2.475(6)
Ni(4)–2Ni(1)	2.625(8)	Ni(4)–2Ni(1)	2.716(7)
Ni(4)–U	3.073(9)	Ni(4)–U	3.104(8)
Ni(5)–1P(3)	1.616(10)	Ni(5)–1As(3)	1.612(9)
Ni(5)–1P(2)	2.327(9)	Ni(5)–1As(2)	2.434(5)
Ni(5)–2P(3)	2.490(9)	Ni(5)–2As(3)	2.525(7)
Ni(5)–1Ni(4)	0.469(9)	Ni(5)–1Ni(4)	0.612(10)
Ni(5)–4Ni(5)	2.490(10)	Ni(5)–4Ni(5)	2.525(7)
Ni(5)–U	3.565(10)	Ni(5)–U	3.714(9)

in the square pyramids, and Ni(1), Ni(2) and Ni(5) in the tetrahedral positions. Both these types of nickel atom sites remind us of those of the Fe_2P-type structure.

In view of the occupation of a given coordination polyhedron, the general formula of the $U_6Ni_{20}Pn_{13}$ compounds can be presented as follows [6]: $U_6(Pri)Ni_2(Tr)Ni_3(Pyr)Ni_{15}(Tet)Pn_{13}$. The very short distances of Ni(5)–Pn(3) and Ni(4)–Ni(5) are the distances between crystallographic sites which are only about half (and not simultaneously) occupied. In fact, Ni(4) and Ni(5) correspond to a splitting of a unique 6h position, which was used in the refinement [3] to account for the very large delocalization of the corresponding nickel atom. Also the partial occupancy for P(3) together with the large thermal factors for these atoms show that this structure is characterized by strong disorder along the hexagonal axis, so that the compounds should exist over some homogeneity domain. Hence, if we take into account the values of the refined occupancy factors given in Table 2, the calculated formulae of the crystals studied are $U_6Ni_{20.2}P_{12.8}$ and $U_6Ni_{19.8}P_{12.7}$, which are close to the ideal formula with the atomic ratio 6:20:13.

These compounds are now the subject of other physical property measurements.

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