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Letter to the Editors

Characterization of the new uranium–nickel alloy $U_{10}Ni_{13}$

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Abstract

The crystal structure of $U_{10}Ni_{13}$ was investigated from single crystal X-ray diffraction data. This phase, which was formerly designated by the formulation U_7Ni_9, crystallizes in a new structure type (monoclinic, space group C2/m, $a = 7.6602(3)$ Å, $b = 13.0801(5)$ Å, $c = 7.6498(3)$ Å, $\beta = 108.875(2)°$). There are 20 uranium atoms in the unit cell, distributed in 8j, 8j and 4i Wyckoff positions and 26 nickel atoms occupying 8j, 8j, 4i, 4i, 2a Wyckoff positions. In the first coordination sphere, the U–U distances range from 2.753(1) to 3.075(2) Å and the U–Ni distance ranges from 2.648(3) to 2.866(3) Å. $U_{10}Ni_{13}$ does not order magnetically at low temperature. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Uranium alloys are of great interest for nuclear technology as well as for fundamental research. Most of the binary intermetallic systems were investigated for the first reason many years ago, and binary U–M phase diagrams have been constructed with nearly all other M metals [1]. In many cases however, some uncertainty remains on parts of these diagrams, when the mentioned binary phases have not been fully characterized crystallographically.

Seven intermediate phases have been reported to form in the U–Ni system: $U_6Ni, U_7Ni_9, U_5Ni_7, UNi_2$, UNi_5, and phases denoted ε and δ [1]. The unit cell parameters and structure types have been reported in 1950 [2] for three of them: U_6Ni, UNi_2 and UNi_5, and only space group and unit cell parameters were given for the phase ε [3]. To our knowledge, no information concerning the characteristics of the phases designated U_5Ni_7 and U_7Ni_9 have been published up to now. In this work, structural and magnetic studies of the latter compound are presented.

2. Experimental

The initial materials used were uranium ingots (depleted uranium platelets 99.8%, Merck, surface cleaned in diluted HNO_3 before use) and nickel wire (99%, Strem). The samples were prepared by arc melting the two elements under high purity argon atmosphere. The buttons were inverted and remelted twice to ensure complete homogeneization. The alloys were then wrapped in tantalum foil and annealed à 740 °C for two weeks in quartz tubes sealed under vacuum. The single crystal X-ray diffraction data were collected on a NONIUS kappa CCD four circle diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). The orientation matrix and the unit cell parameters were derived from the first 10 measured frames of the data using the program DENZO [4].

Magnetic measurements were performed in the range 5–300 K using a SHE–VTS squid magnetometer.

3. Crystal structure determination

The studied alloy, with previously reported composition U_7Ni_9, was found to crystallize in the monoclinic system with the following lattice parameters:

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Table 1
Crystallographic data

Composition	$U_{10}Ni_{13}$
Space group	C2/m (No. 12)
Lattice parameters	$a = 7.6602(3)$ Å $b = 13.0801(5)$ Å $c = 7.6498(3)$ Å $\beta = 108.875(2)°$
Cell volume (Å^3)	725.26 Å^3
Formula units per cell	$Z = 2$
Formula weight (g)	3143.5
Density (calculated) (Mg/m^3)	14.39
Crystal size (mm^3)	$0.05 \times 0.07 \times 0.08$
Wavelength	0.71073 Å
Scan range (θ) (deg)	$2.81 < \theta < 40.21°$
Range in h k l	$0 \leqslant h \leqslant 13, 0 \leqslant k \leqslant 23,$ $-13 \leqslant l \leqslant +12$
Linear absorption coefficient (mm^{-1})	127.51
Total number of reflections	2247
Reflections observed (> 2)	1597
Goodness-of-fit	1.162
Conventional residual (F)	$R_f = 0.0540$
Weighted residual, $w = I/\sigma^2(F)$	$R_w = 0.1286$

$a = 7.6602(3)$ Å, $b = 13.0801(5)$ Å, $c = 7.6498(3)$ Å, $\beta = 108.875(2)°$. The space group extinctions led to the possible space groups C2, Cm or C2/m, among which the centrosymmetric C2/m group was found to be the proper one for this structure.

The positions of uranium and of some of the nickel atoms were determined by direct methods using SHELXS-97 [5] and subsequent difference Fourier analysis revealed the positions of the remaining nickel atoms. There are 20 uranium atoms in the unit cell, which are distributed on three Wyckoff positions (8j, 8j, 4i) of the C2/m space group. The 26 nickel atoms are distributed on five Wyckoff positions (8j, 8j, 4i, 4i, 2a,). The atomic positions, occupation factors and thermal parameters were refined using SHELXL-97 [5]. All the atomic sites were found to be fully occupied, leading thus to the crystallographic formula $U_{20}Ni_{26}$. This composition is slightly richer in nickel than the corresponding one previously reported with U_7Ni_9 formula, (equivalent to $U_{21}Ni_{27}$). Crystal data and refinement results for $U_{10}Ni_{13}$ are given in Table 1. Atomic and thermal parameters are given in Table 2, and the main interatomic distances are gathered in Table 3. The atomic parameters have been standardized using the programme STIDY [6].

4. Structure description

$U_{10}Ni_{13}$ crystallizes with a new structure type, and no clear relation with existing structural types was found. Fig. 1 shows projections of the structure along the *b*- and *a*-axes, revealing the formation of metallic planes perpendicularly to the [1 0 1] and [0 1 0] directions.

The U(1) atom is surrounded by four nickel atoms: two Ni(3), one Ni(1) and one Ni(2) forming a tetrahedron, and by four uranium atoms: one U(3), one U(1) and two U(2) forming an other tetrahedron, with distances ranging from 2.753 for U(1)–U(1) to 2.892 Å for U(1)–U(2). The U(2) atom is one vertex of a tetrahedron, built up with three nickel atoms (one Ni(1), one Ni(3)

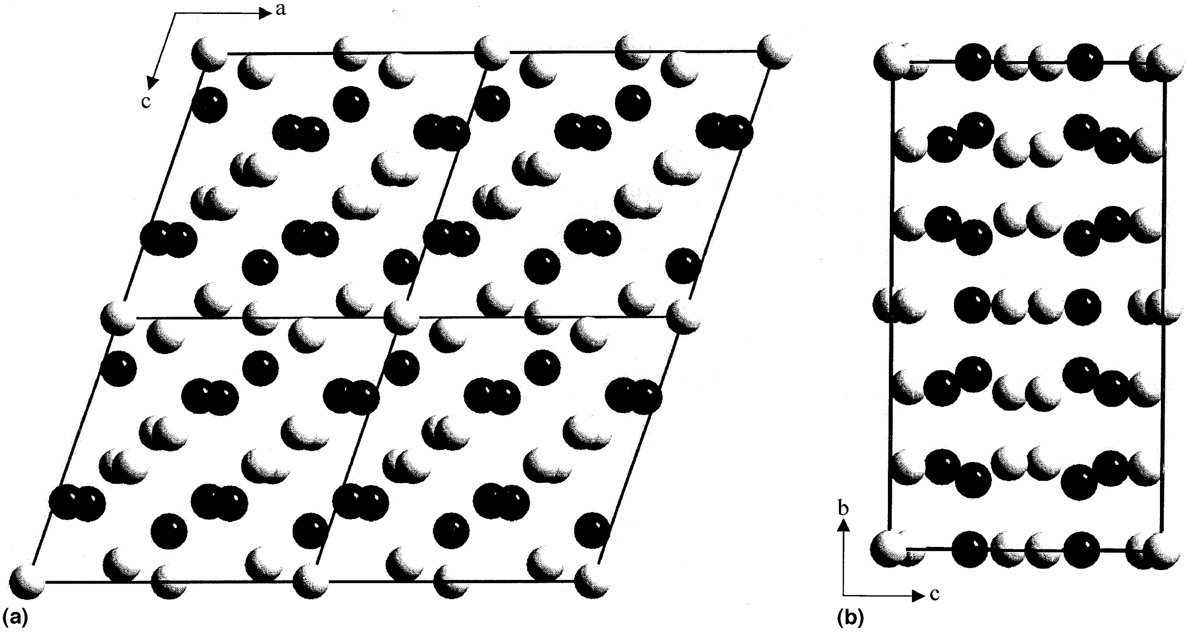

Fig. 1. (a) Projection of the structure along the *b*-axis; (b) projection of the unit cell along the *a*-axis.

Table 2
Atom parameters for $U_{10}Ni_{13}$

Atoms	U1	U2	U3	Ni1	Ni2	Ni3	Ni4	Ni5
Site	8j	8j	4i	8j	4i	8j	2a	4i
Occupation	1	1	1	1	1	1	1	1
x	0.0616(1)	0.4569(1)	0.3807(1)	0.3232(1)	0.6833(4)	0.1894(2)	0	0.2241(4)
y	0.3318(1)	0.3599(1)	0	0.1776(2)	0	0.1678(2)	0	0
z	0.1901(1)	0.3026(1)	0.2952(1)	0.4377(2)	0.0664(4)	0.0640(2)	0	0.5649(4)
U11	0.010(1)	0.011(1)	0.016(1)	0.011(1)	0.011(1)	0.012(1)	0.014(2)	0.017(1)
U22	0.010(1)	0.013(1)	0.010(1)	0.012(1)	0.007(1)	0.012(1)	0.012(2)	0.011(1)
U33	0.007(1)	0.009(1)	0.010(1)	0.008(1)	0.010(1)	0.009(1)	0.019(2)	0.009(1)
U12	−0.0004(9)	0.002(1)	0	−0.001(1)	0	0.001(1)	0	0
U13	0.003(1)	0.002(1)	0.006(1)	0.003(1)	0.003(1)	0.004(1)	0.006(1)	0.006(1)
U23	0.0001(9)	−0.0001(9)	0	−0.001(1)	0	0.001(1)	0	0
Ueq (Å^2)	0.009(1)	0.011(1)	0.012(1)	0.010(1)	0.009(1)	0.011(1)	0.015(1)	0.012(1)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a*^2\,\mathrm{U11} + k^2b*^2\,\mathrm{U22} + l^2c*^2\,\mathrm{U33} + 2hka*b*\mathrm{U12} + 2hla*c*\mathrm{U13} + 2klb*c*\mathrm{U23}$. The isotropic displacement factor exponent takes the form: $-8\pi^2\mathrm{Ueq}[\sin(\theta)/\lambda]^2$.

Table 3
Interatomic distances (Å) in the first coordination spheres

Ni1–1Ni1	2.538(4)	Ni3–1Ni4	2.588(2)	Ni5–1Ni2	2.677(4)	U2–1Ni5	2.686(2)
Ni1–1Ni1	2.565(4)	Ni3–1Ni3	2.653(4)	Ni5–2U2	2.686(2)	U2–1Ni3	2.687(2)
Ni1–1U3	2.663(2)	Ni3–1U1	2.665(2)	Ni5–2Ni1	2.720(2)	U2–1Ni1	2.703(2)
Ni1–1U1	2.697(2)	Ni3–1U2	2.687(2)			U2–1U1	2.849(1)
Ni1–1U2	2.703(2)	Ni3–1U1	2.698(2)	U1–1Ni3	2.665(2)	U2–1U2	2.875(1)
Ni1–1Ni3	2.710(2)	Ni3–1Ni1	2.710(2)	U1–1Ni2	2.679(2)	U2–1U1	2.892(2)
Ni1–1Ni5	2.720(2)	Ni3–1Ni2	2.718(2)	U1–1Ni1	2.697(2)		
		Ni3–1Ni3	2.746(2)	U1–1Ni3	2.698(2)	U3–1Ni2	2.648(3)
Ni2–1Ni4	2.634(3)			U1–1U1	2.753(1)	U3–2Ni1	2.663(2)
Ni2–1U3	2.648(3)	Ni4–4Ni3	2.588(2)	U1–1U2	2.849(1)	U3–1Ni5	2.702(3)
Ni2–1Ni2	2.659(5)	Ni4–2Ni2	2.634(3)	U1–1U3	2.851(1)	U3–2U1	2.851(1)
Ni2–1Ni4	2.677(4)			U1–1U2	2.892(1)	U3–1U3	3.075(2)
Ni2–2U1	2.679(2)						
Ni2–2Ni3	2.718(2)						

and one Ni(5)) and form also with three uranium atoms (two U(1) and one U(2)) an other tetrahedron. The U(2)–U bonds are rather homogeneous with distances of 2.849 and 2.892 for U(2)–2U(1) and 2.875 Å for U(2)–U(2). The environment of U(3) can be viewed as a tetrahedron built up from two Ni(1), one Ni(5) and one Ni(2). It is capped by one Ni(5), two U(1) at 2.851 Å and one U(3) at 3.075 Å. All the above mentioned interatomic U–U distances are similar to those existing in uranium metal and are indicative of effective metal–metal bonds.

5. Magnetic properties

Fig. 2 shows the temperature variation of the magnetic susceptibility of $U_{10}Ni_{13}$ measured in a field of 0.5 T in the temperature range 5–300 K.

$U_{10}Ni_{13}$ exhibits a weakly temperature dependant paramagnetic behaviour, with a slight decrease of the

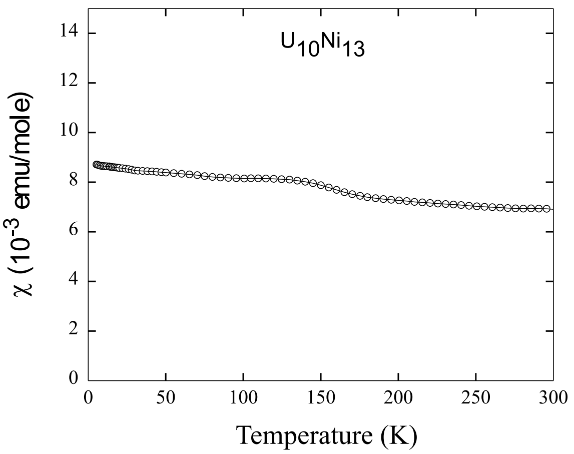

Fig. 2. Thermal variation of the magnetic susceptibility of $U_{10}Ni_{13}$.

susceptibility from 87×10^{-4} emu mol^{-1} at 5 K to 69×10^{-4} emu mol^{-1} at 300 K and a steeper variation around 150 K. The absence of local magnetic moment is related to a strong delocalization of 5f electrons, via a large 5f–5f orbital overlap in agreement with Hill's plot [7] as well as via the hybridization of the U(5f) with the Ni(3d) electron, as indicated by the short above mentioned intermetallic distances.

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