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Crystal structure refinements and magnetic behavior of U_6Ni, UNi_5, UNi_2 and the substitution derivative $UNi_{1.7}Si_{0.3}$

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The crystal structures of the binaries U_6Ni, UNi_2 and UNi_5 have been refined for the first time from single crystal data. U_6Ni crystallizes in the tetragonal system, U_6Mn type, s.g. *I*4/*mcm*, with lattice parameters *a* = 10.3835(8) Å, *c* = 5.1565(4) Å. The uranium atoms occupy 8*h* (U1) and 16*k* (U2) Wyckoff positions, and the Ni atoms a 4*a* position. UNi_5 crystallizes in the cubic $AuBe_5$ type, s.g. $F\bar{4}3m$, with *a* = 6.7958(6) Å and the following atom site occupations: U in 4*a*, Ni1 in 16*e* and Ni2 in 4*c*. UNi_2 crystallizes in the hexagonal $MgZn_2$ type, s.g. $P6_3/mmc$, with *a* = 4.9701(4) Å, *c* = 8.2527(8) Å. Uranium occupies a 4*f* position and the nickel atoms are in 2*a* (Ni1) and 6*h* (Ni2) positions. The shortest interatomic U-U distances are 2.619(2) Å in U_6Ni, 3.026(1) Å in UNi_2, and 4.805(1) Å in UNi_5. UNi_2 shows itinerant ferromagnetism below 25 K, which vanishes with substitution of silicon for nickel.

Uranium compounds / Intermetallics / Crystal structure / Magnetic properties

1. Introduction

The crystal structure types of the binary uranium-nickel intermetallics U_6Ni, UNi_2 and UNi_5 are known, but to our knowledge their crystal structures had not been previously refined from single crystal data. This work is part of our program concerning a more detailed characterization of the binary uranium intermetallics. We have recently shown by single crystal X-ray diffraction [1-3] that the uranium-nickel compounds formerly reported as U_7Ni_9 and U_5Ni_7 [4] in fact correspond to $U_{10}Ni_{13}$ and $U_{11}Ni_{16}$ with original structure types, and that the phases denoted ε-δ corresponds to UNi_{5-x} ($0.9 < x < 1$) with the hexagonal $CaCu_5$ type.

2. Experimental

The elements used were depleted uranium plates (99.8% purity), cleaned in diluted HNO_3 before use), and nickel wire (99.5% purity). Samples with nominal compositions were prepared by direct melting of the two elements in an arc-furnace, under partial pressure of purified argon atmosphere. The buttons were inverted and remelted two times to ensure complete homogenization. Single crystals suitable for X-ray data collection were obtained by annealing U_6Ni and UNi_2 in sealed quartz tubes for two weeks at 790°C and 820°C, respectively.

The single crystal X-ray diffraction data were collected on a Nonius Kappa CCD diffractometer. The unit-cell parameters and the orientation matrix were initially determined from the first ten measured frames of the data, and refined during the indexing and the intensity integration process of all the recorded images, using the program DENZO of the Kappa CCD software package [5]. All structure refinements were carried out using SHELXL-97 [6]. Crystal data and structure refinement parameters for all the studied compounds are gathered in Table 1. Magnetization measurements were performed using a SHE Squid magnetometer in the temperature and field ranges 2-300 K and 0-3 T.

3. Results

3.1. U_6Ni

Single crystals suitable for X-ray data collection were obtained by annealing a sample of U_6Ni in a sealed quartz tube for two weeks at 790°C, which is the reported peritectic decomposition temperature [4]. U_6Ni crystallizes in the tetragonal system, U_6Mn type, s.g. *I*4/*mcm*, with lattice parameters *a* = 10.3835(8) Å, *c* = 5.1565(4) Å. The uranium atoms occupy 8*h* (U1) and 16*k* (U2) Wyckoff positions, and the Ni atoms a 4*a* position (Table 2a). Interatomic

Table 1 Crystal data and structure refinement parameters.

	U_6Ni	UNi_5	UNi_2	$UNi_{1.7}Si_{0.3}$
Space group	*I*4/*mcm* (No 140)	$F\bar{4}3m$ (No 216)	$P6_3/mmc$ (No 194)	$P6_3/mmc$ (No 194)
Lattice parameters (Å)	a = 10.3835(8)	a = 6.7958(6)	a = 4.9701(4)	a = 5.1312(3)
	c = 5.1565(3)		c = 8.2527(8)	c = 7.8207(6)
Cell volume (Å^3)	555.96	313.85	176.55(3)	178.33(2)
Formula units per cell	Z = 4	Z = 4	Z = 4	Z = 4
Formula weight (g)	1486.9	531.6	355.4	346.2
Density (calculated) (Mg/m^3)	17.76	11.25	13.37	12.89
Crystal size (mm^3)	0.04 × 0.04 × 0.05	0.05 × 0.05 × 0.05	0.04 × 0.06 × 0.04	0.05 × 0.06 × 0.06
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Scan range (deg.)	3 < θ < 35°	5 < θ < 35°	5 < θ < 35°	5 < θ < 35°
Range in *hkl*	-11≤ h ≤16	-10≤ h ≤10	-7≤ h ≤8	0≤ h ≤8
	-8≤ k ≤11	-10≤ k ≤10	-7≤ k ≤8	-7≤ k ≤0
	-8≤ l ≤ 8	-10≤ l ≤ 8	-12≤ l ≤ 13	0≤ l ≤ 12
Linear absorption coefficient (mm^{-1})	177.26	80.48	112.02	123.14
Total number of reflections	1161	1429	2607	263
Independent reflections	359	94	173	179
Reflections observed (>2σ)	268	93	149	158
Goodness-of-fit	0.874	1.231	1.069	1.191
Conventional residual (F)	R_f = 0.0389	R_f = 0.0194	R_f = 0.0340	R_f = 0.0396
Weighted residual, w = I/σ^2 (F)	R_w = 0.0946	R_w = 0.0413	R_w = 0.0838	R_w = 0.1001

U-U distances (Table 3a) are as short as those in uranium metal: U2-U2 = 2.619(2) Å, U1-U1 = 2.821(3) Å, U1-U2 = 2.872(7) Å, leading to a nearly temperature-independent paramagnetism in the range 2-300 K. The value of the magnetic susceptibility is 29 10^{-4} emu/mole at 300 K. This compound was reported to be exhibit superconductivity below T_c = 0.33 K [7].

3.2. UNi_5

Single crystals of UNi_5 could be obtained by annealing an arc-melted sample at 1300°C for 5 hours under vacuum in a high-frequency furnace. UNi_5 crystallizes in the cubic system, $AuBe_5$ type, s.g. $F\bar{4}3m$, with a = 6.7958(6) Å and atom site occupations: U in 4*a*, Ni1 in 16*e* and Ni2 in 4*c* (Table 2b). The shortest interatomic distances (Table 3b) are U-U = 4.805(1) Å, and U-Ni1 = 2.820(1) Å. UNi_5 is a quasi temperature-independent paramagnet from 2 K to 300 K with a value of the magnetic susceptibility of 25 10^{-3} emu/mole at 300 K. In UNi_5, the 5f delocalization results from the U(5f)-Ni(3d) hybridization.

3.3. UNi_2 and $UNi_{1.7}Si_{0.3}$

Single crystals of UNi_2 were obtained after annealing an arc-melted stoichiometric sample at 820°C for one week. Refinement of the crystal structure confirmed that UNi_2 crystallizes with the hexagonal $MgZn_2$ type (s.g. $P6_3/mmc$), whereas the other Laves phases UM_2 with M = Mn, Fe, Co crystallize in the cubic $MgCu_2$ type. The lattice parameters are: a = 4.9701(4) Å, c = 8.2527(8) Å. Uranium occupies a 4*f* position and the nickel atoms are in 2*a* (Ni1) and 6*h* (Ni2) positions (Table 2c). The shortest interatomic distances are U-U = 3.026(1) Å and U-Ni1 = 2.909(1) Å (Table 3c). In agreement with previous reports [8], our magnetization measurements on polycrystalline annealed samples indicated weak ferromagnetism, with a Curie temperature T_C = 25 K (Fig. 1). The value of the magnetization is 0.095 μ_B at 5 K under 3 T. A rather large anisotropy of the magnetization was revealed by magnetization on single crystal [9]. Considering that the U-U distances are far below the Hill limit (3.40 Å) implying a very large 5f electron delocalization, the unusual magnetic correlations observed in UNi_2 have been interpreted in terms of itinerant ferromagnetism, associated with a large orbital moment of the 5f electrons [10].

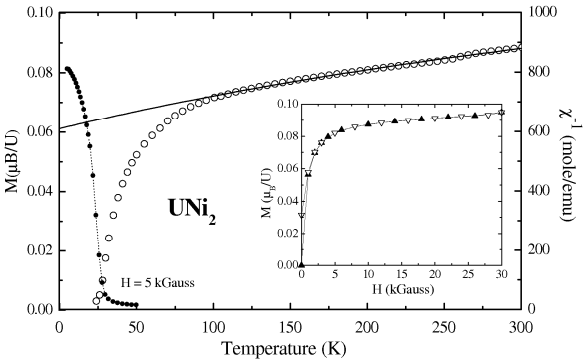

Fig. 1 Thermal variation of the magnetization (filled circles) and of the reverse susceptibility (empty circles) under 5 kGauss for UNi_2. Inset: Magnetization as a function of the applied field at T = 5 K. Filled triangles = field up; empty triangles = field down.

Table 2

(a) Atomic position parameters for U_6Ni

Atom	Site	*x*	*y*	*z*	U_{eq} (Å^2)
U1	8*h*	0.09603(6)	0.59603(6)	0	0.0137(3)
U2	16*k*	0.10622(6)	0.21545(6)	0	0.0130(2)
Ni	4*a*	0	0	1/4	0.0136(8)

(b) Atomic position parameters for UNi_5

Atom	Site	*x*	*y*	*z*	U_{eq} (Å^2)
U	4*a*	0	0	0	0.0137(3)
Ni1	16*e*	0.62385(2)	0.62385(2)	0.62385(2)	0.0168(4)
Ni2	4*c*	1/4	1/4	1/4	0.0244(7)

(c) Atomic position parameters for UNi_2

Atom	Site	*x*	*y*	*z*	U_{eq} (Å^2)
U	4*f*	1/3	2/3	0.55813(7)	0.0193(4)
Ni1	2*a*	0	0	0	0.0130(2)
Ni2	6*h*	0.1658(2)	0.3316(4)	1/4	0.0156(5)

(d) Atomic position parameters for $UNi_{1.7}Si_{0.3}$

Atom	Site	*x*	*y*	*z*	U_{eq} (Å^2)
U	4*f*	1/3	2/3	0.5699(1)	0.0138(4))
M1[a]	2*a*	0	0	0	0.0130(2)
Ni2	6*h*	0.1679(3)	0.3358(6)	1/4	0.0121(5)

[a] M1 = 39%Ni+61%Si

Table 3

(a) Main interatomic distances (Å) in U_6Ni

U1	- 1U1	2.821(3)	U2	- 1U2	2.619(2)	Ni - 2Ni	2.579(9)
	- 2U2	2.872(7)		- 2Ni	2.808(6)	- 8U2	2.808(6)
	- 4U2	3.240(6)		- 1U1	2.872(7)		
	4U1	3.260(7)		- 2U2	3.037(7)		

(b) Main interatomic distances (Å) in UNi_5

U	- 12Ni1	2.820(1)	Ni1	- 3Ni1	2.381(3)
	- 4Ni2	2.943(1)		- 3Ni1	2.425(3)
	- 12U	4.805(1)		- 3Ni2	2.815(1)
				- 3U	2.820(1)
Ni2	- 12Ni1	2.815(1)			
	- 4U	2.943(1)			

(c) Main interatomic distances (Å) in UNi_2 (M1 = Ni) and $UNi_{1.7}Si_{0.3}$ (M1 = 39%Ni+61%Si)

		UNi_2	$UNi_{1.7}Si_{0.3}$
U	- 3M1	2.909(1)	3.012(1)
	- 3Ni2	2.924(1)	2.902(2)
	- 6Ni2	2.946(1)	2.927(1)
	- 3U	3.026(1)	3.158(1)
	- 1U	3.167(1)	2.817(2)
M1	- 6Ni2	2.509(1)	2.459(2)
	- 6U	2.909(1)	3.012(1)
Ni2	- 2Ni2	2.472(3)	2.547(5)
	- 2Ni2	2.498(3)	2.584(5)
	- 2M1	2.509(1)	2.459(2)
	- 2U	2.924(1)	2.902(2)
	- 4U	2.947(1)	2.927(1)

A complete investigation of the isothermal section at T = 900°C of the U-Ni-Si ternary system [11] revealed that Si may substitute for Ni in UNi_2, forming the solid solution $UNi_{2-x}Si_x$ up to x = 0.3, keeping the $MgZn_2$ type. Refinement of the crystal structure of a single crystal having the limiting composition $UNi_{1.7}Si_{0.3}$ and lattice parameters a = 5.1312(3) Å, c = 7.8207(6) Å (Table 1) showed that Si replaces 61% of the Ni1 atoms on the 2*a* position. This substitution induces an increase of the U-M1 distance from 2.909(1) Å to 3.012(1) Å and a concomitant change of the shortest U-U distances, from 3.026(1) Å to 3.158(1) Å and from 3.167(1) Å to 2.817(2) Å (Table 2). Magnetic measurements for $UNi_{1.7}Si_{0.3}$ indicated a nearly temperature-independent paramagnetism from 2 to 300 K, with a value of the magnetic susceptibility of $9 \cdot 10^{-4}$ emu/mole at 300 K. Consequently, the ferromagnetic correlations are strongly dependant on the modification of the band structure induced by the changes of the U-U distances from UNi_2 to $UNi_{1.7}Si_{0.3}$.

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