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Crystal Structure and Magnetic Behavior of the Laves-Type Phases $U_4Mo_5Si_3$ and $U_4Cr_6Si_2$[1]

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$U_4Mo_5Si_3$ and $U_4Cr_6Si_2$ have been synthesized by argon arc-melting the elemental combinations and annealing at 1400°C. The homogeneity domains of $U_4Mo_{5+x}Si_{3-x}$ and $U_4Cr_{6+y}Si_{2-y}$ have been established by X-ray powder and single-crystal diffraction analysis and range from $x = 0$ to 1 and from $y = -0.5$ to 1. Single-crystal X-ray studies have shown that the transition metal and the silicon are both distributed on the two sites occupied by zinc in the Laves phase $MgZn_2$ (6*h* and 2*a* positions in *P*6₃/*mmc*). Magnetic investigations of these compounds revealed temperature-independent paramagnetism as a result of the very short uranium–uranium distance found in the structure determinations.

INTRODUCTION

As part of our systematic study of phase relationships in the U–Mo–Si system at 1400°C (1), we have prepared the ternary uranium molybdenum silicide $U_4Mo_5Si_3$. The existence of this compound and also $U_4Fe_6Si_2$, $U_4Cr_6Si_2$, $U_4Mn_5Si_3$, and $U_4Co_6Si_2$, which have the $MgZn_2$ structure type (2, 3), was reported in the 1960s by Sikirica and Ban (4) and Kusma and Nowotny (5, 6). In this structural type (space group $P6_3/mmc$), magnesium is in the 4*f* position and zinc occupies crystallographic sites of multiplicity 6 and 2. It was postulated that, in $U_4Cr_6Si_2$, the transition metal occupies a 6*h* position and silicon a 2*a* position. On the other hand, the formulation $U_4Mo_5Si_3$ suggests a disorder on the 6*h* and 2*a* positions and therefore the existence of a homogeneity domain. In the present paper we describe the preparation, the structural chemistry, and the magnetic behavior of $U_4Mo_5Si_3$ and $U_4Cr_6Si_2$.

EXPERIMENTAL DETAILS

The pseudo-ternary phases $U(Mo_xSi_{1-x})_2$ and $U(Cr_ySi_{1-y})_2$ have been synthesized by argon arc-melting ingots of the elements. In order to avoid oxidation due to slightly surface-oxidized molybdenum and chromium, those two metals were first melted individually once. To ensure homogeneity, the alloy pellets were turned over and remelted several times. The weight losses were below 0.5 wt%. Various compositions ranging between 4 : 6 : 2 and 4 : 5 : 3 were prepared and a homogeneity domain was revealed for the molybdenum and the chromium compounds by X-ray diffraction. Small single crystals were obtained by heating the arc-melted pellets at high temperature (~1500°C) for few hours followed by slow cooling.

Single-crystal X-ray diffraction studies were performed using an automatic Enraf–Nonius CAD 4 four-circle diffractometer with graphite monochromated Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). The lattice parameters were obtained by least-squares refinement of the setting angles of 25 reflections. Details of the intensity data collection and crystallographic data are summarized in Table 1. Intensities were corrected for Lorentz and polarization effects. After isotropic refinement, an empirical absorption correction was performed by means of the DIFABS program (7). All calculations were carried out on a VAX 3100 microcomputer using the SDP crystallographic software packages (8). The structure was refined in the space group $P6_3/mmc$, with the positions of all atoms being assigned by analogy with the structure of $MgZn_2$.

STRUCTURAL CHEMISTRY

Crystal Structure of $U_4Mo_5Si_3$

The uranium atom was found to occupy the 4*f* position ($\frac{1}{3}$, $\frac{2}{3}$, z). The electronic densities calculated from a difference Fourier analysis revealed some statistical distribution of molybdenum and silicon on the 6*h* (x, $2x$, $\frac{1}{4}$ and the 2*a* (0, 0, 0) crystallographic sites: four molybdenum and two silicon atoms are located on the 6*h* site and one molybdenum and silicon atom on the 2*a* site. This result is in disagreement with that previously obtained from powder data (6), in which an ordered distribution of transition metals and silicon over the 6*h* and 2*a* positions, respectively, was

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[1] Dedicated to Professor Robert Troc on the occasion of his 60th birthday.

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TABLE 1
Crystallographic Data for $U_4Mo_5Si_3$ ($MgZn_2$ Type)

Space group	$P6_3/mmc$
Lattice parameters (from CAD 4) (Å)	$a = 5.3729(4)$; $c = 8.527(2)$
Cell volume (Å^3)	213.18(4)
Formula units per cell	1
Formula weight (g)	1516.1
Calculated density (Mg m^{-3})	11.81
Crystal size (mm)	0.10 × 0.07 × 0.10
Scan range (θ)	$1° \leq \theta \leq 40°$
Range in h, k, l	$0 \leq h \leq 9$; $0 \leq k \leq 9$; $0 \leq l \leq 15$
Linear absorption coefficient ($MoK\alpha_1$) (mm^{-1})	79.03
Total number of reflections	568
Reflections with $I > \sigma(I)$	434
Goodness of fit	0.669
Unweighted residual (R_F)	0.018
Weighted residual (R_w), $w = 1/\sigma^2(F)$	0.023

TABLE 3
Interatomic Distances (Å) for $U_4Mo_5Si_3$ (X = Mo or Si)

U–3X1	3.0926(3)	X1–2X1	2.612(1)	X2–6X1	2.662(1)
6X1	3.1086(6)	2X2	2.662(1)	6U	3.1536(1)
1U	3.1271(8)	2X1	2.761(1)		
3X2	3.1536(1)	2U	3.0926(3)		
3U	3.3036(3)	4U	3.1086(6)		

assumed. After refinement, the final residual value was $R = 0.018$. The final position and thermal parameters are listed in Table 2 and selected interactomic distances are presented in Table 3.

The crystal structure of $U_4Mo_5Si_3$ is shown in Fig. 1. It can be seen that the alternating layers of molybdenum (or silicon) and uranium follow the sequence $X2$–U–$X1$–U–$X2$–U–$X'1$–U–$X2$ (X = molybdenum or silicon). The uranium atom is surrounded by 16 atoms, which form a Friauf polyhedron (2, 9) previously described by Komura and Tokunaga in (10). The 6h and 2a sites have icosahedral coordinations.

One of the interesting aspects of this structure is the existence of a very short uranium–uranium distance (3.127 Å), close to that existing in metallic uranium (3.10 Å). This implies a strong delocalization of the 5f electrons of uranium, and thus one can expect a temperature-independent paramagnetic behavior for this compound.

Crystal Structure of $U_4Cr_6Si_2$

The structures of three crystals grown from mixtures with nominal starting compositions 4:6:2, 4:6:2, and 4:5:3 have also been refined from single-crystal X-ray diffraction data. The results are summarized in Tables 4, 5, and 6. Rather poor quality of crystals 1 and 3 resulted in weaker diffraction intensities and higher final R values. Structure factor tables are available from the authors upon request.

In each case, the uranium atom is situated in the 4f position ($\frac{1}{3}$, $\frac{2}{3}$, z). The site occupancy refinements for the 6h (x, 2x, $\frac{1}{4}$) and 2a (0, 0, 0) positions gave the following atomic distributions:

	Crystal 1	Crystal 2	Crystal 3
6h site (X1)	5 Cr + 1 Si	6 Cr	4.7 Cr + 1.3 Si
2a site (X2)	1 Cr + 1 Si	1 Cr + 1 Si	0.8 Cr + 1.2 Si
Formula	$U_4Cr_6Si_2$	U_4Cr_7Si	$U_4Cr_{5.5}Si_{2.5}$

Taking into account these structural results, we can assume that the homogeneity domain spreads at least from U_4Cr_7Si to $U_4Cr_{5.5}Si_{2.5}$. As with $U_4Mo_5Si_3$, uranium–uranium metal bonds are also inferred in these crystals, with the shortest U–U distance (2.939 Å) existing for the composition $U_4Cr_{5.5}Si_{2.5}$.

MAGNETISM

The magnetic properties have been studied in the temperature range 5–300 K using a SQUID magnetometer and are summarized in Fig. 2.

$U_4Mo_5Si_3$

As shown in Fig. 2, $U_4Mo_5Si_3$ exhibits a temperature-independent paramagnetism between 10 and 300 K (χ_m ~

TABLE 2
Atomic Parameters for $U_4Mo_5Si_3$ (X = Mo or Si)

Atom	Position	x	y	z	B (Å^2)	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U	4f	$\frac{1}{3}$	$\frac{2}{3}$	0.06663(4)	0.411(3)	0.00468(6)	β_{11}	0.00146(3)	β_{11}	0	0
X1	6h	0.8287(1)	0.6574	$\frac{1}{4}$	0.51(1)	0.0066(2)	0.0046(3)	0.00168(7)	β_{22}	0	0
X2	2a	0	0	0	0.39(1)	0.0051(3)	β_{11}	0.0010(1)	β_{11}	0	0

Note. $B = (\frac{4}{3})\Sigma_{i,j}\beta_{i,j}a_i \cdot a_j$. The coefficients for anisotropic thermal measurements are expressed as $\exp -[h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23}]$. Standard deviations in the least significant digits are given in parentheses.

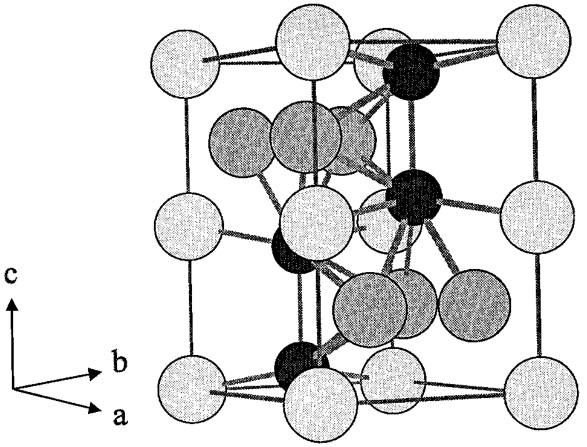

FIG. 1. Perspective view of the crystal structure of $U_4Mo_5Si_3$ (X = Mo or Si; $X1$, dark gray circles; $X2$, gray circles; U, black circles). Bonding distances shorter than 3.2 Å around uranium atoms are shown.

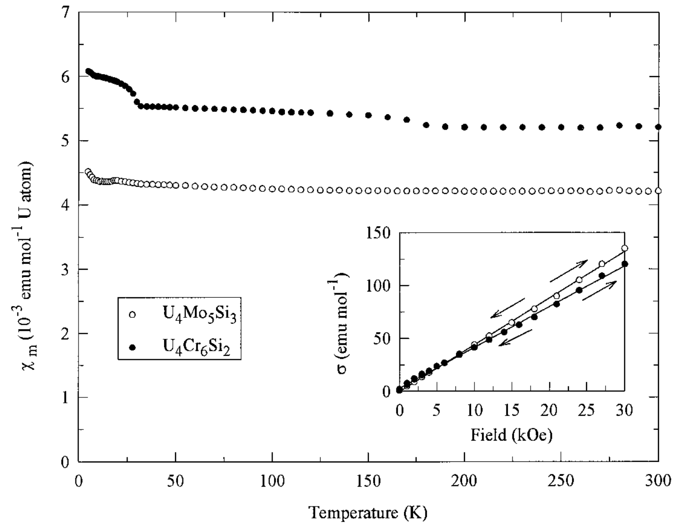

FIG. 2. Susceptibility per uranium atom vs temperature for $U_4Mo_5Si_3$ and $U_4Cr_6Si_2$. Magnetization vs field is also shown.

4.3×10^{-3} emu/mole). As stated above, this behavior is consistent with the existence of very short uranium–uranium bonds in this structural type. The small increase of the susceptibility below 10 K is probably due to the presence of magnetic impurities. The absence of magnetic interactions at low temperature is confirmed by the curve of magnetization versus magnetic field at 5 K (Fig. 2, insert), which is linear and reversible.

$U_4Cr_6Si_2$

The magnetic behavior of $U_4Cr_6Si_2$ (as well as of $U_4Cr_{5.5}Si_{2.5}$) is similar to that found for $U_4Mo_5Si_3$, with a temperature-independent paramagnetism of 5.5×10^{-3} emu/mole. The slight variation of the susceptibility at about 170 K and below 25 K is thought to be due to impurities.

CONCLUSION

The parameters of the atomic positions of the Laves-phase-type compounds $U_4(Mo_xSi_{1-x})_8$ and $U_4(Cr_xSi_{1-x})_8$ have been refined, and it has been found that, in both cases, the transition metal and the silicon are distributed over the two sites occupied by zinc in the Laves phase

TABLE 4
Crystallographic Data for U_4Cr_7Si, $U_4Cr_6Si_2$, and $U_4Cr_{5.5}Si_{2.5}$ ($MgZn_2$ Type)

Composition	U_4Cr_7Si	$U_4Cr_6Si_2$	$U_4Cr_{5.5}Si_{2.5}$
Space group	$P6_3/mmc$	$P6_3/mmc$	$P6_3/mmc$
Lattice parameters (Å) (from CAD 4)	a = 5.128(1)	a = 5.133(1)	a = 5.177(2)
	c = 8.275(4)	c = 8.253(2)	c = 8.147(2)
Cell volume (Å^3)	188.46(9)	188.35(5)	189.06(4)
Formula units per cell	1	1	1
Formula weight (g)	1344.2	1320.3	1308.3
Calculated density (Mg m^{-3})	11.84	11.64	11.49
Crystal size (mm)	0.10 × 0.06 × 0.06	0.10 × 0.10 × 0.10	0.07 × 0.06 × 0.05
Scan range (θ)	$1° \le \theta \le 40°$	$1° \le \theta \le 40°$	$1° \le \theta \le 40°$
Range in h, k, l	$0 \le h \le 9$	$-9 \le h \le 9$	$-9 \le h \le 9$
	$0 \le k \le 9$	$0 \le k \le 9$	$0 \le k \le 9$
	$0 \le l \le 14$	$0 \le l \le 14$	$0 \le l \le 14$
Linear absorption coefficient (Mo$K\alpha_1$) (mm^{-1})	89.49	89.54	88.03
Total number of reflections	505	918	918
Reflections with $I > \sigma(I)$	358	660	708
Goodness of fit	0.986	1.298	2.101
Unweighted residual (R_F)	0.065	0.038	0.104
Weighted residual (R_w)	0.083	0.053	0.107

TABLE 5
Atomic Parameters for U_4Cr_7Si, $U_4Cr_6Si_2$, and $U_4Cr_{5.5}Si_{2.5}$ (X = Cr or Si)

Atom	Site	x	y	z	B (Å^2)	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
					U_4Cr_7Si						
U	4f	$\frac{1}{3}$	$\frac{2}{3}$	0.0653(2)	0.24(1)	0.0033(2)	β_{11}	0.0007(1)	β_{11}	0	0
X1	6h	0.8304(7)	0.6608	$\frac{1}{4}$	0.57(7)	0.008(1)	0.005(2)	0.0020(5)	β_{22}	0	0
X2	2a	0	0	0	0.11(9)	0.002(2)	β_{11}	0.0002(9)	β_{11}	0	0
					$U_4Cr_6Si_2$						
U	4f	$\frac{1}{3}$	$\frac{2}{3}$	0.0651(1)	1.069(9)	0.0134(2)	β_{11}	0.00397(7)	β_{11}	0	0
X1	6h	0.8300(6)	0.6600	$\frac{1}{4}$	1.20(6)	0.016(1)	0.015(2)	0.0043(3)	β_{22}	0	0
X2	2a	0	0	0	0.89(6)	0.013(2)	β_{11}	0.0025(5)	β_{11}	0	0
					$U_4Cr_{5.5}Si_{2.5}$						
U	4f	$\frac{1}{3}$	$\frac{2}{3}$	0.0696(2)	0.57(1)	0.0071(2)	β_{11}	0.0022(1)	β_{11}	0	0
X1	6h	0.8289(6)	0.6578	$\frac{1}{4}$	0.72(7)	0.009(1)	0.008(2)	0.0029(5)	β_{22}	0	0
X2	2a	0	0	0	0.6(1)	0.006(2)	β_{11}	0.003(1)	β_{11}	0	0

Note. $B = (\frac{4}{3})\Sigma_{i,j}\beta_{i,j}a_i \cdot a_j$. The coefficients for anisotropic thermal measurements are expressed as exp $-[(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23}]$. Standard deviations in the least-significant digits are given in parentheses.

$MgZn_2$. The homogeneity domain which results from this fact is larger in the system U–Cr–Si ($U_4Cr_{5.5}Si_{2.5}$–U_4Cr_7Si) than in the system U–Mo–Si ($U_4Mo_5Si_3$–$U_4Mo_6Si_2$) (1). The magnetic properties of these compounds are consistent with their structural characteristics: the very short uranium–uranium distances involve a very strong 5f–5f overlap, with metallic bonding and therefore the absence of a localized moment. As a consequence, measurements at very low temperature (<1 K) should be interesting to check for the possible occurrence of superconductivity.

TABLE 6
Interatomic Distances (Å) for U_4Cr_7Si, $U_4Cr_6Si_2$, and $U_4Cr_{5.5}Si_{2.5}$ (X = Cr or Si)

		U_4Cr_7Si			
U–6X1	2.985(3)	X1–2X1	2.520(1)	X2–6X1	2.559(1)
3X1	2.987(1)	2X2	2.559(1)	6U	3.010(0)
3X2	3.010(0)	2X1	2.609(1)		
1U	3.057(3)	4U	2.985(3)		
3U	3.152(1)	2U	2.987(1)		
		$U_4Cr_6Si_2$			
U–3X1	2.979(1)	X1–2X1	2.515(1)	X2–6X1	2.558(1)
6X1	2.986(3)	2X2	2.558(1)	6U	3.012(1)
3X2	3.012(1)	2X1	2.618(1)		
1U	3.052(2)	2U	2.979(1)		
3U	3.153(1)	4U	2.986(3)		
		$U_4Cr_{5.5}Si_{2.5}$			
U–U	2.939(3)	X1–2X1	2.520(1)	X2–6X1	2.550(1)
6X1	2.977(3)	2X2	2.550(1)	6U	3.042(0)
3X1	2.983(1)	2X1	2.657(1)		
3X2	3.042(0)	4U	2.977(3)		
3U	3.197(1)	2U	2.983(1)		

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