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Structural Chemistry and Magnetic Behavior of Binary Uranium Silicides

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Binary uranium silicides have been thoroughly reinvestigated with respect to crystal chemistry and magnetic properties; for most compounds, magnetic studies have been carried out at low temperatures for the first time (2 to 300 K, 0 to 5 T). Formation of all known binary silicides has been confirmed: U_3Si, U_3Si_2 (U_3Si_2-type), USi (USi-type), U_3Si_5 (defect AlB_2-type), $USi_{1.88}$ (defect $ThSi_2$-type) and USi_3 (Cu_3Au-type). At the composition $U_3Si_{\sim5}$ three different phases have been observed: the defect AlB_2-type as well as a phase separation into two orthorhombically distorted AlB_2-type related phases. USi_{2-x} with the tetragonal defect $ThSi_2$-type structure at its silicon poor phase boundary was found to be in equilibrium with USi_{2-x} of the orthorhombic defect $GdSi_2$ type. Precise U–U distances have been derived from X-ray single crystal counter data for U_3Si_2, USi, for the AlB_2-type subcell of U_3Si_5, and for $USi_{1.84}$ (defect $ThSi_2$-type). From susceptibility measurements, a band type paramagnetism was observed for U_3Si_2, whereas a temperature independent paramagnetism was confirmed for USi_3. Curie–Weiss paramagnetism was encountered within the investigated temperature range for U_3Si_5 and $USi_{1.88}$. A modified Curie–Weiss law was revealed for USi with the USi-type, whereas ferromagnetic ordering at $T_c = 125$ K was observed for the oxygen stabilized "USi" with the FeB-type. Magnetism of the uranium silicides is discussed as a function of the distant dependent 5*f*–5*f* electron overlap and *d*–*f* electron hybridization. No superconductivity was observed above 2 K.

Introduction

Considerable attention has been devoted to the metal-rich silicides of uranium with respect to the development of new fuel materials for research reactors running on low enriched uranium (*1–3*).

Constitution of the binary system uranium-silicon has been earlier examined by Vaugoyeau *et al.*(*4*) reporting on the formation of six binary compounds: U_3Si, U_3Si_2, USi, U_3Si_5, $USi_{1.88}$, and USi_3. Some ambiguity, however, exists for the monosilicide, which was earlier reported with the FeB-type structure by Zachariasen (*5*), but according to more recent results (*6*) it is considered to be stabilized by small amounts of oxygen and in fact was indicated to be U_8Si_8O (*4*). The true crystallographic cell of pure USi was observed to be tetragonal with a fairly large unit cell volume, but no structure determination was performed (*6*). Most of the uranium silicides crystallize in well known structure types, where the formation of defects was frequently observed, such as for U_3Si_5 (defect AlB_2-type (*4, 5, 7*)) or

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$USi_{1.88}$ (defect α-$ThSi_2$-type (*4, 5, 7, 8*)). Furthermore, inclination to oxygen incorporation resulted in the formation of new oxysilicides $U_6Si_{11}O$ (*9*) or impurity stabilized phases such as "USi" with the FeB-type (U_8Si_8O (*4*)).

Moreover, despite many research groups dealt with the physical properties of the binary silicides of uranium, low temperature data (below LNT) have only been reported for U_3Si and USi_3. Detailed knowledge of the magnetic behavior of the binary U-silicides is of primary importance in ternary investigations of weakly magnetic heavy fermion systems such as UM_2Si_2 with the $ThCr_2Si_2$-type (*10*) or in superconducting uranium-alumino-silicides (*11*). From a preliminary inspection of the interatomic distances available from the structural data for the binary U–Si compounds, rather short U–U distances in the range of ~0.31–0.33 nm were encountered for U_3Si and U_3Si_2 well below the Hill-limit, suggesting delocalization of the 5*f*-U electrons which could promote superconductivity and/or heavy fermion behavior.

All the above mentioned uncertainties motivated a reinvestigation of the crystal chemistry and low temperature magnetic behavior in the binary U–Si system.

Experimental

Samples, each of a total weight of 1 g were prepared by arc melting uranium ingots (depleted uranium platelets 99.9%, E. Merck, Darmstadt, BRD, surface cleaned in diluted HNO_3 prior to use), and compacted mixtures of silicon powder or lumps (Alfa Ventron, Karlsruhe, 99.999% Si) using a nonconsumable 2%-thoriated tungsten electrode on a water cooled copper hearth under Ti/Zr-gettered high purity argon. Weight losses generally were less than 0.5 wt%.

A part of each melted button was annealed in a high vacuum furnace (10^{-4} Pa) using a tungsten substrate. Annealing conditions were 100 hr at 1400°C, 64 hr at 1200°C (U_3Si_2), or 120 hr at 1000°C, monitored by a micro-optical pyrometer which was calibrated against internal standards to a precision of ±20°C. In all cases samples were radiation quenched.

X-ray powder diffraction patterns at room temperature were prepared from all experimental alloys in the as-cast as well as annealed condition whereby samples were crushed in a WC-Co mortar, and ground to fine powders in an agate mortar. X-ray Guinier–Huber photographs (6N-Ge-standard, a_{Ge} = 0.5657906 nm, $CuK\alpha_1$-radiation) were evaluated with respect to the number of the observed phases, their crystal structure, and unit cell dimensions. Precise lattice parameters and standard deviations were obtained from a least squares fit evaluation procedure; powder diffraction intensities were calculated employing the LAZY-PULVERIX program.

Small single crystals of U_3Si_2, USi, U_3Si_5, and $USi_{1.88}$ suitable for X-ray structure refinement were obtained by mechanical fragmentation from arc melted samples annealed at various temperatures in the range from 700 to 1400°C.

Magnetic measurements were performed in the temperature range from 2 to 300 K and from 0 to 5 T, employing a SHE-SQUID magnetometer.

Results and Discussion

1. *Structural Chemistry*

All results as well as the literature data available are presented in Table I.

A refinement of the crystal structure of U_3Si_2 from X-ray counter data confirmed the crystal symmetry and atom positions (see Table II) as earlier reported by Zachariasen (*5*) from powder data. Variation of the occupancy factor for the uranium atoms did not reveal any deviation from ideal stoichiometry. Anisotropic thermal factors have been refined for the two uranium sites showing

TABLE I

CRYSTALLOGRAPHIC DATA OF BINARY URANIUM SILICIDES

Nominal composition	Preparation heat treatm.	Phase analysis	Structure type	Space group	Lattice parameters (in nm)			Volume (nm^3)	Refs.
					a	*b*	*c*		
h-U$_3$Si			AuCu$_3$	*Pm3m*	0.4346	—	—	0.08209	(*12*)
m-U$_3$Si			m-U$_3$Si	*I4/mcm*	0.6029	—	0.8696	0.31609	(*13*)^c
<780°C					0.6029(2)	—	0.8696(3)	0.31609	(*5*)^b
					0.6033(1)		0.8688(1)	0.31622	(*14*)
					0.6033	—	0.8686	0.31614	(*12*)^c
					0.60328	—	0.86907	0.31630	(*15*)
					0.6033	—	0.8690	0.31629	(*14*)
l-U$_3$Si < 120 K			l-U$_3$Si	*Fmmm*	0.8654(2)	0.8549(2)	0.8523(2)	0.63056	(*16*)
U$_3$Si$_2$	1200°C	U$_3$Si$_2$	U$_3$Si$_2$	*P4/mbm*	0.73364(5)	—	0.38900(8)	0.20937(5)	^{a}
					0.73299	—	0.39004	0.20954	(*5*)^b
					0.73297	—	0.39003	0.20954	(*6*)
USi	1400°C	USi	USi	*I4/mmm*	1.061	—	2.442	2.7490	(*6*)
					1.058(3)	—	2.4310(5)	2.72481(5)	^{c}
U$_3$Si$_5$	1400°C	U$_3$Si$_5$	def. AlB$_2$	*P6/mmm*	0.38475(7)	—	0.4074(1)	0.05223(2)	^{a}
					0.3843(1)	—	0.4069(1)	0.05204	(*18*)
					0.3844	—	0.4076	0.05216	(*29*)
U$_{37.5}$Si$_{62.5}$	1400°C	U$_3$Si$_5$^{b}	def. AlB$_2$	*P6/mmm*	0.3851(1)	—	0.4069(4)	0.05227(5)	^{a}
		U$_3$Si$_5$	def. AlB$_2$	*P6/mmm*	0.3842(6)	—	0.4036(5)	0.0516(1)	
U$_{37.5}$Si$_{62.5}$	1000°C	"U$_3$Si$_5$"^{b}	dist. AlB$_2$	*Pmmm*	0.3846(3)	0.6674(8)	0.4074(2)	0.1046(1)	^{a}
		"U$_3$Si$_5$"	dist. AlB$_2$	*Pmmm*	0.3893(4)	0.6718(9)	0.4035(4)	0.10553	
U$_{36.8}$Si$_{63.2}$	1000°C	"U$_3$Si$_5$"^{b}	dist. AlB$_2$	*Pmmm*	0.3858(2)	0.6663(5)	0.4072(1)	0.1047(1)	^{a}
		"U$_3$Si$_5$"	dist. AlB$_2$	*Pmmm*	0.3897(4)	0.6735(7)	0.4035(4)	0.1059(2)	
U$_{36.8}$Si$_{63.2}$	1400°C	"U$_3$Si$_5$"^{b}	dist. AlB$_2$	*Pmmm*	0.3864(3)	0.6660(5)	0.4073(3)	0.1048(1)	^{a}
		"U$_3$Si$_5$"	dist. AlB$_2$	*Pmmm*	0.38930(8)	0.6717(4)	0.4042(1)	0.10567(7)	
U$_{36}$Si$_{64}$	1000°C	USi$_{2-x}$	def. ThSi$_2$	$I4_1/amd$	0.39423(9)	—	1.3712(15)	0.2131(2)	^{a}
		USi$_{2-x}$	def. GdSi$_2$	*Imma*	0.3953(1)	0.3929(2)	1.3656(44)	0.2121(7)	
USi$_{1.88}$	1400°C	USi$_{2-x}$	def. ThSi$_2$	$I4_1/amd$	0.39457(4)	—	1.3739(7)	0.2139(1)	^{a}
USi$_{1.88}$	1000°C	USi$_{2-x}$	def. ThSi$_2$	$I4_1/amd$	0.39378(7)	—	1.3729(6)	0.2129(1)	^{a}
					0.3948	—	1.367	0.21307	(*7*)
					0.398(3)	—	1.374(8)	0.217	(*5*)^b
USi$_2$	1400°C	USi$_{2-x}$ + (USi$_3$)	def. ThSi$_2$	$I4_1/amd$	0.39406(7)	—	1.3778(7)	0.2139(1)	^{a}
USi$_2$	metastable	USi$_2$	ThSi$_2$	$I4_1/amd$	0.3922	—	1.4154	0.21707	(*8*)
					0.3930	—	1.406	0.21716	(*7*)
USi$_2$	low temp.	USi$_2$	AlB$_2$	*P6/mmm*	0.4028(1)	—	0.3852(1)	0.05412	(*7*)
U$_{22}$Si$_{78}$	arc	USi$_3$^{b}	Cu$_3$Au	*Pm3m*	0.40353(4)	—	—	0.06572(1)	^{a}
		Si$_{\text{trac.}}$		*Fd3m*	0.54303(9)	—	—	0.16013(5)	
USi$_3$		USi$_3$	Cu$_3$Au	$Pm\bar{3}m$	0.40353	—	—	0.06571	(*20*)
					0.403	—	—	0.06545	(*21*)
					0.40348(8)	—	—	0.06568	(*11*)

[a] This work, arc means: as cast condition.

[b] Calculated from kX units.

[c] Expansion coefficient: α_0 760°C = $(0.0171T + 8.7) \times 10^{-6}$ (*12*); average linear expansion coefficient: $\alpha = 7.2 \times 10^{-6}$ K^{-1} (range 160 to 300 K) (*16*).

large vibrations along the *c*-axis for U1 consistent with long interatomic U1–U1 distances. The crystallographic data for U$_3$Si$_2$ are listed in Table II.

The structure of the monosilicide USi has been resolved recently (*29*) confirming the unit cell earlier adopted by (*6*) from a preliminary single crystal study. Careful preparation without any traces of oxygen always led to a large tetragonal cell as suggested by Vaugoyeau *et al.* (*4*). The FeB-type "USi," as reported by Zachariasen (*5*), only was obtained when oxygen was present (adding of U$_3$O$_8$ or presence of air during arc melting) and therefore seems to be "impurity" stabilized. For this compound, the attempt to prepare it in single-phase condition failed. Therefore, an alternative way to produce

TABLE II

CRYSTALLOGRAPHIC DATA FOR U_3Si_2 (X-RAY SINGLE CRYSTAL COUNTER DATA)
U_3Si_2-type structure, Space group: $P4/mbm$-No. 127, origin at $\bar{1}$, $Z = 2$

Atom	site	Positional parameters			$B_{\mathrm{equiv.}}$	
		x	y	z	($nm^2 \times 10^2$)	occ.
U1	$2a$	0	0	0	2.04(3)[a]	1.0
U2	$4h$	0.1821(1)	0.6821(−)	1/2	0.65(1)[b]	1.0
Si	$4g$	0.3841(9)	0.8841(−)	0	0.7(1)	1.0

Residual values: $R_F = 0.038$, $R_w = 0.043$ (for 178 $F_{\mathrm{obs.}} > 3\sigma$)
Lattice Parameters: $a = 0.73314(9)$, $c = 0.39001(8)$ nm, $V = 0.2096$ nm^3.

Interatomic distances (in nm)

U1–6 U1	0.3900	U2–2 U2	0.3894	Si–2 U1	0.2941
U1–8 U2	0.3315	U2–2 U2	0.3799	Si–2 U2	0.2862
U1–4 Si	0.2941	U2–2 U2	0.3776	Si–4 U2	0.2968
		U2–2 Si	0.2862	Si–1 Si	0.2403
		U2–4 Si	0.2968		

[a] Anisotropic thermal parameters: $B11 = 0.91(4)$, $B33 = 4.3(1)$, $B12 = 0$.

[b] Anisotropic thermal parameters: $B11 = 0.82(2)$, $B33 = 0.31(2)$, $B12 = -0.27(4)$.

it from U_3Si_2, arc melted USi (Vaugoyeau-type) and U_3O_8 by sintering samples with the overall composition $U_8Si_8O_x$ ($1.4 < x < 2.8$) in sealed quartz tubes at a temperature of 1000°C was performed. But also with this method, no pure phase of the Zachariasen-type could be obtained.

As far as the compounds U_3Si_5 (AlB_2-type or derivative) and $USi_{1.88}$ ($ThSi_2$-type) are concerned, we observed significant deviations from the information available (*5, 17–19*), in particular with respect to their crystal structures and their range of existence in the phase diagram.

We usually observed U_3Si_5 in the form of two coexisting and virtually isostructural phases, whose relative volume fraction was found to vary with composition in a narrow region of existence. At uranium-rich compositions these two phases were obtained in coexistence with USi, at Si-rich concentrations with USi_{2-x} (see also Table I). At temperatures $T = 700$ and 1000°C both phases showed a small but significant orthorhombic distortion from the hexagonal AlB_2-type lattice geometry, whereas in samples at the exact composition U_3Si_5, which have been annealed at temperatures of 1400°C and above, the intensity of the X-ray pattern of the second phase decreases with increasing temperature. Thus only one phase is revealed at temperatures $T \geq 1400$°C, which seemed to be consistent with the hexagonal but defect AlB_2-type structure. The typical lattice distortion seen in X-ray Guinier powder patterns can be successfully indexed on the basis of an orthorhombic unit cell according to $a = a_0$, $b = a_0\sqrt{3}$, $c = c_0$, where a_0, b_0, and c_0 are the unit cell dimensions of the AlB_2-parent lattice. The X-ray powder patterns of samples annealed at high temperatures (≥1400°C), however, presented some difficulties in refining the lattice parameters due to extensive line broadening. Even with high resolution Guinier photographs we were unable to distinguish between a possible two-phase mixture of two nearly isoparametric and nearly isostructural compounds or a single phase condition with rather broadened peaks of a hexagonal lattice. The situation has some correspondence

(a) with similar results obtained on the orthorhombically distorted Er_3Si_5 (*25*) and/or

(b) with the phase separation into two virtually isostructural phases of practically identical composition as observed recently in the disilicides of the light rare earths (*26, 27*).

Heavily exposed rotation single crystal X-ray photographs taken along [100] and [001] on several single crystal fragments obtained from alloys at a nominal composition U_3Si_5 which were annealed at various temperatures between 700 and 1400°C, in all cases undoubtedly revealed the formation of a fourfold superstructure along the c-axis with respect to the AlB_2-type base cell. There were, however, no indications for superstructure formation along [100]. With respect to the exceedingly small orthorhombic distortions obtained from the Guinier powder data (see Table I), $0.002 < 1 - b/(a\sqrt{3}) < 0.005$, the resolution of the Weissenberg photographs within the limits of error was insufficient to reveal significant deviations from a hexagonal symmetry; the reflections of the superstructure layers, however, showed heavy streaking effects proving the absence of long range ordering of the silicon defects. Due to these smeared out type of intensities, proper recording on a four circle diffractometer was unsuccessful and merely represented limited information on the subcell. Refinement based on the AlB_2 type subcell yielded a residual value of $R_F = 0.038$ for 358 $F_{obs.} > 3\sigma$ and a silicon defect corresponding to a formula $USi_{1.70}$.

The crystallographic behavior of the USi_{2-x} phase $USi_{1.88}$ deriving from the $ThSi_2$-type is essentially resembling the U_3Si_5 case. Whenever the compound $USi_{1.88}$ was observed in coexistence with USi_3, a well crystallized X-ray pattern with sharp reflections was obtained, which was easily indexed on the basis of the socalled disordered tetragonal USi_{2-x}-type (*5, 7*) (see Table I). Refinement of single crystal counter data essentially confirmed the $ThSi_2$-type symmetry earlier reported from powder data (*5*). In good agreement with X-ray powder analyses on $USi_{1.88}$ by (*6*), our refinement of the occupancy of the silicon atoms in the 8e sites corresponds to the chemical formula of $USi_{1.84}$ without indications for vacancy ordering. The crystallographic data of $USi_{1.84}$ have been listed in Table III. X-ray Guinier patterns of alloys with ca. 64 at.% Si revealed a system of reflections suggesting a mixture of two closely related structure types. In contrast to the case of the two U_3Si_5-phases, the coexistence of two virtually isostructural phases with the tetragonal defect $ThSi_2$-type cannot be assured for USi_{2-x}. The powder pattern was completely indexed as a two-phase system consisting of (a) the tetragonal defect $ThSi_2$-type and (b) the orthorhombically distorted defect $GdSi_2$-type (see Table I) as recently encountered in the U–Al–Si ternary (*28*).

The fully ordered as well as stoichiometric USi_2 with the $ThSi_2$-type and/or the AlB_2-type reported earlier (*7, 8*) could not be retrieved from any of our experiments.

Due to its peritectic formation, the compound USi_3 was prepared with a slight excess of silicon ($U_{22}Si_{78}$). Therefore traces of Si have been observed in the Guinier X-ray-powder pattern, which could be indexed completely as the Cu_3Au-type structure known for USi_3. Refinement of the lattice parameters revealed no significant difference with the various values known from literature (*11, 20, 21*).

2. *Magnetic Properties*

The results of our susceptibility measurements are summarized in Table IV and in Figs. 1–5 presenting the reciprocal susceptibilities versus temperature.

U_3Si. U_3Si has been previously reported to undergo a superconducting transition at

TABLE III

Crystallographic Data for $USi_{1.84}$ (X-ray Single Crystal Counter Data)
Defect $ThSi_2$-type structure, Space group: $I4_1/amd$-No. 141, origin at $\bar{1}$, $Z = 4$

	Positional parameters				
Atom site	x	y	z	B(nm^2 × 10^2)	occ.
U 4*a*	0	3/4	1/8	0.62(1)	1.0
Si 8*e*	0	1/4	0.7086(7)	1.9(2)	0.92

Residual values: $R_F = 0.036$, $R_w = 0.047$ (for 119 $F_{obs.} > 3\sigma$)
Lattice Parameters: $a = 0.3937(1)$, $c = 1.3654(8)$ nm, $V = 0.2116$ nm^3.

Interatomic distances (in nm)

U–4 U 0.3937	U–8 Si 0.3009	Si–1 Si 0.2284
U–4 U 0.3940	U–4 Si 0.3006	Si–2 Si 0.2269

$T_c < 0.56$ K (*23*) but the sample was poorly characterized; therefore, the possibility that this transition is merely due to U-metal or U_3Si_2 cannot be ruled out.

U_3Si_2. No literature data are available to us concerning the magnetic properties of this compound. Our measurements on the SQUID magnetometer show a practically temperature independent paramagnet with a slight linear increase of the susceptibility from 31 × 10^{-4} emu mole^{-1} at 5 K to 35 × 10^{-4} emu mole^{-1} at 300 K (see Fig. 1), which is interpreted as band-type paramagnetism. We could not detect any superconducting transitions in our samples down to 2 K, but as critical temperatures of superconducting uranium containing compounds are generally of the order of 1 K or below, compounds

TABLE IV

Magnetic Properties of the Binary Uranium Silicides

Compound	Type of magnetism	$T_{C,N,S}$ (K)	μ_{eff} (BM)	Θ_P (K)	χ_0 (10^6 cm^3/mole)	Ref.
U_3Si	TIP	—	—	—	2310	(*23*)
		—	—	—	1900	(*24*)
U_3Si_2	TIP				3500	[a]
USi	MCW	—	1.84	−302	836	[a]
"USi"	F	125	—	—	—	[a]
	F	120	—	—	—	(*24*)
U_3Si_5	CW	—	3.23	−267	—	[a]
			3.40	−320	—	(*19*)
$USi_{1.88}$	CW	—	3.53	−410	—	[a]
USi_3	TIP	—	—	—	600	[a]
					600	(*11*)
					660	(*22*)

Note. CW = Curie Weiss Law, MCW = Modified Curie Weiss Law, TIP = Temperature Independent Paramagnetism, F = Ferromagnetism.

[a] This work.

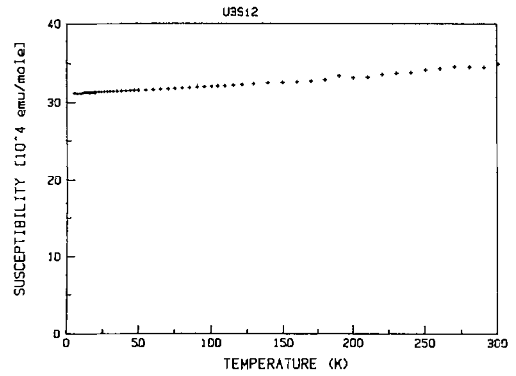

FIG. 1. Temperature dependence of the magnetic susceptibility for U_3Si_2.

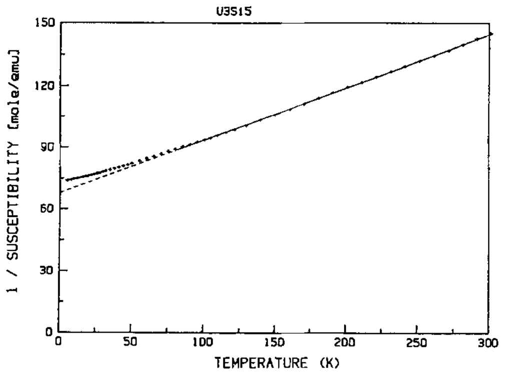

FIG. 3. Temperature dependence of the reverse susceptibility for U_3Si_5 (def. AlB_2-type).

with U–U distances below the Hill limit (ca. 0.34 nm) have to be characterized in the very low temperature range. U–U distances are as short as 0.287 nm for U_3Si (*16*) and 0.332 nm for U_3Si_2 (see Table IV).

USi. Misiuk and Trzebiatowski (*24*) reported ferromagnetic ordering below T_c = 120 K for the uranium monosilicide "USi"; we confirm this magnetic behavior ($T_c \sim 125$ K) for a sample prepared by arc melting of U + Si + UO_2, composed mainly of the Zachariasen-type oxygen stabilized "USi" (claimed to be isotypic with the FeB(?)-type) and small amounts of U_3Si_5. The magnetic susceptibility of the pure form of USi in the tetragonal USi-type (see above), however, does not reveal magnetic ordering down to 2 K and is fitted with a modified Curie–Weiss (M.C.W.) law $\chi = \chi_0 + C/(T - \theta)$ from which a value $\mu_{\text{eff}} = 1.84\ \mu_B/U$ for the paramagnetic moment has been derived (Fig. 2). The particularly small paramagnetic moment of uranium is in good correspondence with the large amount of uranium atoms (60%) involved in U–U bonds shorter than 0.340 nm (see Ref. (*29*)).

U_3Si_5 (defect AlB_2-type). The variation of the susceptibility of U_3Si_5 versus temperature was fitted with a simple Curie–Weiss law based on a value $\mu_{\text{eff}} = 3.23\ \mu_B$

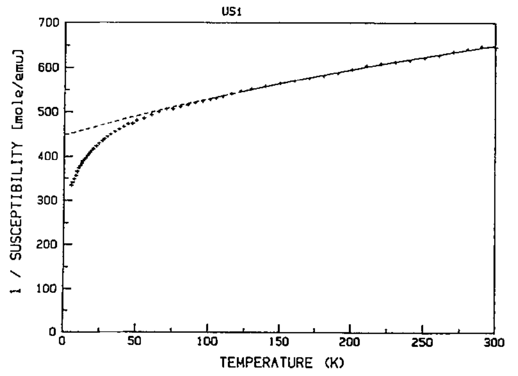

FIG. 2. Temperature dependence of the reverse susceptibility for USi.

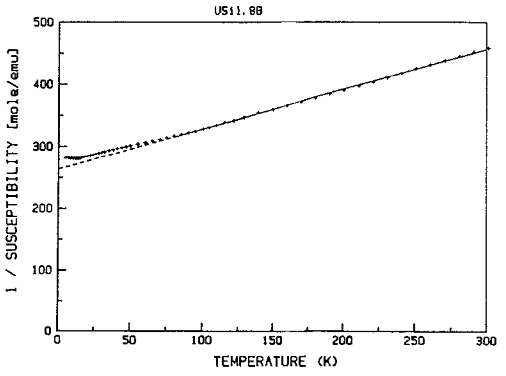

FIG. 4. Temperature dependence of the reverse susceptibility for $USi_{1.88}$ (def. $ThSi_2$-type).

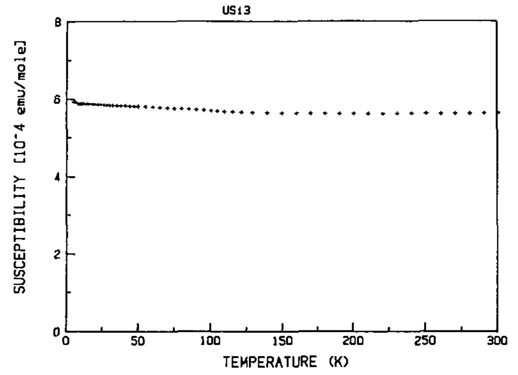

FIG. 5. Temperature dependence of the magnetic susceptibility for USi_3.

(Fig. 3), which is usually found for uranium in the tetravalent state with some crystal field splitting of the ground term. A slight positive deviation is observable below 100 K on the $\chi^{-1} = f(T)$ curve, and no magnetic transition occurs down to 2 K. These results are in general agreement with those earlier reported for this compound (*19*). The magnetic behaviour corresponds with the U–U distances of 0.385 nm being beyond the Hill limit.

$USi_{1.88}$ (defect $ThSi_2$-type). The susceptibility of this compound closely fits a Curie–Weiss law (Fig. 4) with $\mu_{eff} = 3.53\ \mu_B/U$, which is close to the theoretical U^{4+} ($5f^2$) free ion value ($^3H_4$, $\mu_{eff} = 3.58\ \mu_B$) consistent with the U–U distances of 0.394 nm being beyond the Hill limit. A slight positive deviation also occurs below 100 K and a constant Van Vleck type paramagnetism, as typical for singlet ground state systems, is observed below 10 K.

USi_3. Our results confirm earlier data (*11*, *22*) insofar as this compound exhibits a temperature independent Pauli type paramagnetism with a susceptibility value $\chi_0 = 6 \times 10^{-4}$ emu/mole; see Table I and Fig. 5.

Binary uranium silicides follow the general U–U distance dependency as derived from the Hill plot, insofar as the nonmagnetic or even superconducting property of the uranium-rich silicides U_3Si and U_3Si_2 is subdued to strong $5f$–$5f$ overlap, whereas the uranium disilicides U_3Si_5 and $USi_{1.88}$ exhibit localized $5f$-moments. The compound USi holds an interesting intermediate position due to its rather widespread nearest neighbor U–U distances (from 0.3004 to 0.3609 nm (*29*)) crossing the Hill limit, and therefore USi partly develops localized states. USi_3, the compound richest in Si, is a special case where despite its large U–U distances (U–U = 0.4035 nm) no localized $5f$-states are found as a result of strong p–f and d–f hybridization (*11*).

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