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Influence of the Silicon Composition on the Crystallographic Properties of the New Ferromagnetic Ternary Silicides $U_2Fe_{17-y}Si_y$ ($3.3 \leq y \leq 4.5$) and $U_2Co_{15}Si_2$

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After melting and quenching, the ternary silicides $U_2Fe_{17-y}Si_y$ exist for $3.3 \leq y \leq 4.5$ but they partially decompose after annealing at 850–900°C. Their crystal structure, determined by X-ray diffractometry on both single crystals and powder, derives from the hexagonal Th_2Ni_{17}-type but depends strongly on the silicon content. For $y = 3.7$ some uranium sites are partially replaced by pairs of iron atoms and conversely. This structure shows some similarities to that observed for the binary compound Ho_2Fe_{17}. On the other hand, for $y = 4.2$, all the uranium atoms and pairs of iron atoms are statistically distributed. In contrast, the ternary silicide $U_2Co_{15}Si_2$, which is obtained as single phase after annealing at 850°C, adopts the Th_2Ni_{17}-type structure. In all compounds, iron or cobalt atoms of the pair are never substituted by silicon atoms. © 1993 Academic Press, Inc.

Introduction

It is worth noting that no binary compound such as UFe_{12} or U_2Fe_{17} is known since the material having the highest iron content in the uranium–iron system is UFe_2 (66.7% Fe atoms) (*1*). However, the addition of a small amount of silicon, used as a stabilizing element, allowed us to obtain new ferromagnetic materials such as $UFe_{10}Si_2$ with the tetragonal $ThMn_{12}$-type structure (76.9% Fe atoms and $T_C = 650 \pm 10$ K) and $U_2Fe_{13}Si_4$ deriving from the hexagonal Th_2Ni_{17}-type structure (68.4% Fe atoms and $T_C = 505 \pm 10$ K) (*2, 3*).

In this paper a crystallographic study concerning (i) the $U_2Fe_{17-y}Si_y$ system, showing the influence of the silicon content on the crystal structure, and (ii) the $U_2Co_{15}Si_2$ ternary silicide is reported.

Experimental Procedure

The alloys were prepared by direct melting of high purity (at least 3N) uranium, iron or cobalt, and silicon in an induction levitation furnace under a purified argon atmosphere. The obtained ingots were quenched, then annealed in evacuated quartz tubes at 850°C for 1 week. The samples were systematically examined before and after annealing by microprobe analysis in order to check their homogeneity and composition.

The structures were determined by X-ray diffractometry using both powder samples and single crystals. Precise lattice parameters were obtained at room temperature by a least-squares refinement method with the help of Guinier X-ray powder data using both monochromatized $CuK\alpha_1$-radiation and an internal standard of silicon. X-ray powder diffraction data on $U_2Fe_{17-y}Si_y$ ($y = 3.7$ and 4.2) and $U_2Co_{15}Si_2$ were collected on a Philips PW 1050 diffractometer using a Bragg–Brentano geometry with a copper target and a takeoff angle of 6°. In order to avoid problems of preferred orientation of the crystallites, a finely ground (<25 μm) powder of the sample was ran-

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domly scattered over a substrate made of the same sample. The powder diffraction patterns were scanned in steps of 0.02° (2θ) from 10° to 115° with a constant counting time of 40 sec. These patterns were analyzed using the Rietveld profile refinement method (*4*). Single crystal investigations were made on $U_2Fe_{17-y}Si_y$ with $y = 3.7$ and 4.2 with an automatic diffractometer (CAD 4 Enraf–Nonius) using graphite-monochromated Mo$K\alpha$ radiation. All calculations for the structure refinement were made with the SHELX 76 program (*5*). The atomic scattering factors for neutral atoms and anomalous dispersion corrections were taken from the International Tables for X-Ray Crystallography (*6*).

Results and Discussion

Formation of the Compounds

The $U_2Fe_{17-y}Si_y$ alloys were prepared for $0 \leq y \leq 5$. Microprobe analysis performed on the melted and quenched samples showed that only the compounds corresponding to $3.3 \leq y \leq 4.5$ were obtained as single phases which, in this composition range, decompose partially after annealing at 850–900°C leading to $UFe_{10}Si_2$ mainly as a parasitic phase. The products consist of a mixture containing UFe_2, $UFe_{10}Si_2$, and $U_2Fe_{13.7}Si_{3.3}$ for $y < 3.3$ and UFe_2Si_2, FeSi, and $U_2Fe_{12.5}Si_{4.5}$ for $y > 4.5$.

On the other hand, $U_2Co_{15}Si_2$ silicide is prepared as a pure phase by simple melting of the elements and does not decompose after annealing as observed in the case of $U_2Fe_{17-y}Si_y$ compounds.

Structural Properties

(*a*) *$U_2Fe_{17-y}Si_y$ ($3.3 \leq y \leq 4.5$)*. The X-ray powder patterns of these silicides could be indexed on the basis of a primitive hexagonal unit cell similar to that observed for the binary compounds RE_2Fe_{17} (RE = Gd → Er) crystallizing in the Th_2Ni_{17}-type structure (*7*). The lattice parameters of these compounds are given in Table I.

TABLE I

CRYSTALLOGRAPHIC DATA FOR THE $U_2Fe_{17-y}Si_y$ SILICIDES

	Lattice parameters (Å)			
y	a	c	c/a	$V(Å)^3$
3.3	8.330	8.267	0.992	496.8
3.5	8.334	8.234	0.988	495.3
3.7	8.352	8.218	0.984	496.5
4.0	8.359	8.165	0.977	494.1
4.2	8.373	8.162	0.975	495.6
4.5	8.358	8.130	0.973	491.8

The X-ray powder patterns obtained for the compounds with y = 3.3, 3.5, and 3.7 are similar to that calculated for $U_2Fe_{13.3}Si_{3.7}$ assuming that this compound adopts the Th_2Ni_{17}-type structure ($P6_3/mmc$ space group) (Fig. 1). For this calculation, silicon atoms have been distributed statistically between the four different sites 4f, 6g, 12j, and 12k occupied also by the transition element. However, some discrepancies exist between measured and calculated intensities for some reflections since, for instance, the intensities observed for (010), (020), (120), and (022) reflections are either very weak or not observed in the experimental pattern. This result indicates that the $U_2Fe_{17-y}Si_y$ compounds with $3.3 \leq y < 4.0$ crystallize in a structure derived from the Th_2Ni_{17}-type.

For $4 \leq y \leq 4.5$, we observe that the intensity of some characteristic lines of the pattern for the Th_2Ni_{17}-type structure such as (011), (021), or (123) decreases as y increases (Fig. 1). To a first approximation, the main peaks of the X-ray powder patterns of the compounds corresponding to this composition range could be indexed on the basis of the hexagonal unit cell with Gd_2Fe_{17}-type structure ($P6/mmm$ space group) (*8*). Let us mention that in Gd_2Fe_{17} obtained after annealing at 900°C, gadolin-

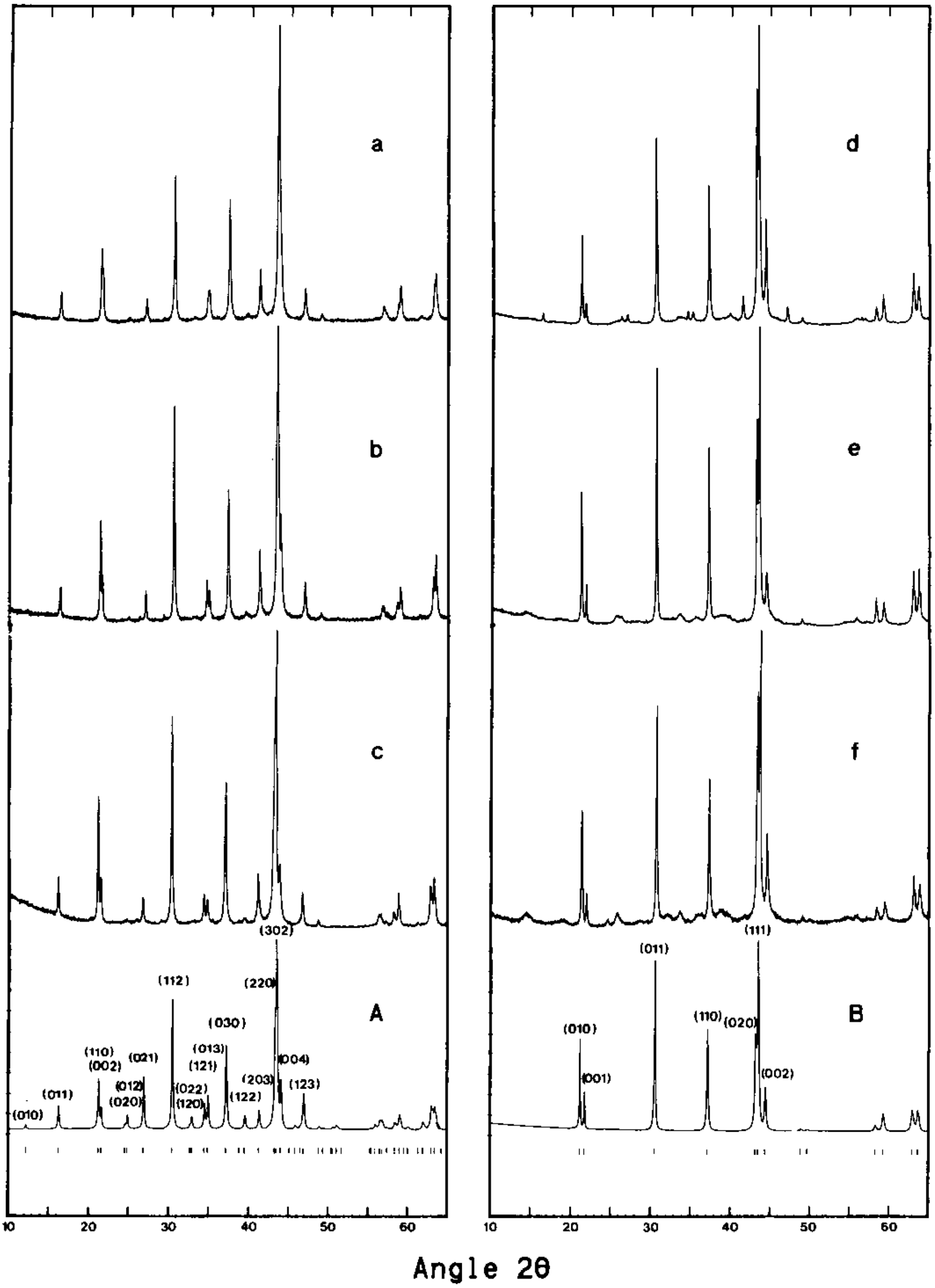

FIG. 1. X-ray powder pattern of $U_2Fe_{17-y}Si_y$ observed for $y = 3.3$ (a), 3.5 (b), 3.7 (c), 4.0 (d), 4.2 (e), and 4.5 (f) and calculated respectively for $y = 3.7$ (A) and 4.2 (B) with the Th_2Ni_{17}- and Gd_2Fe_{17}-type structures.

ium atoms and iron–iron pairs currently referred as "dumbbells" are statistically distributed. Furthermore, the relations between the unit cell parameters of the Th_2Ni_{17} and Gd_2Fe_{17}-type structure are described by

$$a_{Th_2Ni_{17}} = \sqrt{3}\, a_{Gd_2Fe_{17}} \quad \text{and} \quad c_{Th_2Ni_{17}} = 2c_{Gd_2Fe_{17}}.$$

As an example, Fig. 1B shows the X-ray pattern of the $U_2Fe_{12.8}Si_{4.2}$ silicide, calculated on the basis of the Gd_2Fe_{17}-type structure.

The structural properties of the $U_2Fe_{17-y}Si_y$ silicides have been studied on single crystals for the compositions $y = 3.7$ and $y = 4.2$. In all cases, the single crystals have been isolated by mechanical fragmentation from melted and quenched samples.

(*a1*) *$U_2Fe_{13.3}Si_{3.7}$*. A study by X-ray photographic techniques confirms the hexagonal symmetry. Systematic extinctions are observed for (hhl) with $l \neq 2n$, leading to three possible space groups: $P6_3/mmc$, $P6_3mc$, and $P\bar{6}2c$. The intensity of 2874 reflections have been collected in one half of the reciprocal space corresponding to $-15 \leq h \leq 15$, $-15 \leq k \leq 15$, and $0 \leq l \leq 14$. After application of both the Lorentz and polarization corrections and averaging the symmetry equivalent reflections, these data lead to 365 reflections with $F_o^2 > 3\,\sigma(F_o^2)$. (F_o is the observed structure factor). The internal consistency index, $R_{INT} = (\Sigma_j \Sigma_i |F_{oi,j} - F_{oj}|)/\Sigma F_o = 0.065$, confirms the $6/mmm$ Laue class of the hexagonal symmetry.

The structure refinement has been made on the basis of the $P6_3/mmc$ space group, which is that adopted by the Th_2Ni_{17}-type structure (*9*). In this model, the uranium atoms are located in the 2b and 2d sites whereas the iron atoms occupy the 4f, 6g, 12j, and 12k sites. In this case, the value obtained for the R-factor, $R = \Sigma|F_o - F_c|/\Sigma|F_o| = 0.15$, is not satisfying. Furthermore, the difference Fourier map reveals additional electron density (76 $e/Å^3$) due to a heavy atom such as uranium in the 2c site $(\frac{1}{3}\ \frac{2}{3}\ \frac{1}{4})$ located between the two iron atoms described as a "dumbbell" and occupying the 4f site. Correspondingly, some percentage of iron atoms can be inserted in 4e site (0 0 0.1041) which surrounds the 2b site occupied by uranium atoms. The simultaneous occupancy either of the 4f site by iron and the 2c site by uranium or of the 4e site by iron and the 2b site by uranium may be excluded taking into account steric considerations. This indicates that some sites are occupied either by an iron–iron pair or by uranium atoms. After the final refinement, the residual R-factor is 0.066. The occupancy factors, position parameters and equivalent isotropic temperature factors are given in Table IIa. In our calculation, the silicon distribution is not taken into account.

The structure of $U_2Fe_{13.3}Si_{3.7}$ derives, as do those reported for Ho_2Fe_{17} or Lu_2Fe_{17}, from the ideal Th_2Ni_{17}-type structure in which some ordered substitutions occur (*10, 11*). In this type structure, given in Fig. 2, the uranium atoms and "dumbbell" iron sites are located in two planes perpendicular to the c axis: the P plane ($z = \frac{1}{4}$) and the T plane ($z = \frac{3}{4}$). In this view, the Th_2Ni_{17}-type can be described by the following sequence of planes: P, T, P, T, . . . (Figs. 2 and 3a). These planes are separated by other planes containing only the Fe3 (6g site) and Fe6 (12k site) atoms (Fig. 2). But the simultaneous and partial substitutions observed for the $U_2Fe_{13.3}Si_{3.7}$, such as the replacement of U1 (2b site) by an Fe2 (4e)–Fe2 (4e) pair on the one hand, and consequently the substitution of an Fe1 (4f)–Fe1 (4f) pair by U2 (2c site) on the other hand, leads to the existence of a new type of plane S (Fig. 3b). The S plane substitutes both the P and T planes so that the structure of the $U_2Fe_{13.3}Si_{3.7}$ compound can be schematically depicted by the following sequence: (P + εS), (T + εS), (P + εS), (T + εS), . . . (Fig. 3c). We note that $\varepsilon = 21.5\%$ in our final refinement (Table IIa). The S plane can be deduced from the P or T planes either by the translation $\mathbf{p}$ $(-\frac{1}{3}\ \frac{1}{3}\ 0)$ or by the translation $\mathbf{t}$ $(\frac{1}{3}\ -\frac{1}{3}\ 0)$ respectively (Fig. 2).

TABLE II

REFINED STRUCTURAL PARAMETERS USING SINGLE CRYSTAL DATA (a) OR X-RAY POWDER DATA (b) FOR $U_2Fe_{13.3}Si_{3.7}$

		Position parameters				Occupancy		
Atom	Site	x	y	z	$B_{eq.}$ (Å)^2	No. of atoms	%	Site in Th_2Ni_{17}
				(a)				
U1	2b	0	0	$\frac{1}{4}$	0.73(1)	1.57(2)	78.5	2b
Fe2(S)	4e	0	0	0.1041(8)	0.5(7)	0.86(4)	21.5	2b
U2(S)	2c	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	1.7(5)	0.43(2)	21.5	4f
Fe1	4f	$\frac{1}{3}$	$\frac{2}{3}$	0.1070(7)	0.5(1)	3.14(4)	78.5	4f
U3	2d	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{4}$	0.44(6)	2	100	2d
Fe3	6g	$\frac{1}{2}$	0	0	0.5(2)	6	100	6g
Fe4	12j	0.0351(6)	0.668(1)	$\frac{1}{4}$	1.22(8)	9.4(1)	78.3	12j
Fe5(S)	12j	−0.002(1)	0.7018(8)	$\frac{1}{4}$	1.22(8)	2.6(1)	21.7	12j
Fe6	12k	0.1661(6)	0.332(1)	−0.0141(5)	1.4(2)	12	100	12k
				(b)				
U1	2b	0	0	$\frac{1}{4}$	0.30(4)	1.67(1)	83.3	2b
Fe2(S)	4e	0	0	0.1010(7)	0.24(5)	0.67(1)	16.7	2b
U2(S)	2c	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0.30(4)	0.33(1)	16.7	4f
Fe1	4f	$\frac{1}{3}$	$\frac{2}{3}$	0.1010(7)	0.24(5)	3.33(1)	83.3	4f
U3	2d	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{4}$	0.30(4)	2	100	2d
Fe3	6g	$\frac{1}{2}$	0	0	0.24(5)	4.0(1)	66.7	6g
Si1	6g	$\frac{1}{2}$	0	0	0.24(5)	2.0(1)	33.3	6g
Fe4	12j	0.0377(6)	0.675(1)	$\frac{1}{4}$	0.24(5)	6.6(1)	55.0	12j
Si2	12j	0.0377(6)	0.675(1)	$\frac{1}{4}$	0.24(5)	3.4(1)	28.3	12j
Fe5(S)	12j	−0.008(1)	0.696(1)	$\frac{1}{4}$	0.24(5)	2.0(1)	16.7	12j
Fe6	12k	0.1603(7)	0.3206(7)	−0.0174(4)	0.24(5)	10.0(1)	83.3	12k
Si3	12k	0.1603(7)	0.3206(7)	−0.0174(4)	0.24(5)	2.0(1)	16.7	12k

These translations lead to new position parameters for Fe5 (12j) located in the S plane which differ slightly from those determined for Fe4 (12j) located in both P and T planes.

The X-ray powder pattern obtained at room temperature for $U_2Fe_{13.3}Si_{3.7}$ has been analyzed by means of the Rietveld profile refinement technique (Fig. 4). This refinement, with the hypothesis of the structural model given by the single crystal study, leads to a value of the reliability factor R_I of 0.068. The parameters derived from this procedure and summarized in Table IIb are in good agreement with those reported using single crystal determination. In particular, the percentage of replacement, ε, of P and T planes by S planes is about 17%. On the other hand, the fact that silicon atoms occupy only the 6g, 12j, and 12k sites with different occupancy rates, and never the 4e and 4f sites which correspond to the iron "dumbbell" sites, can be understood, in term of steric considerations. Thus, silicon due to its larger atomic radius (r_{Si} = 1.319 Å) compared to that of iron (r_{Fe} = 1.274 Å) (*12*) cannot occupy the iron "dumbbell" sites, for which the iron–iron distances are very short (Fe2–Fe2 = Fe1–Fe1 = 2.449 Å). We must note also that a large number of Si atoms (~4) in 6g and 12k sites are present in planes where U atoms are absent.

(*a2*) $U_2Fe_{12.8}Si_{4.2}$. The Weissenberg and Buerger photographs indicate hexagonal symmetry with a = 4.834(2) Å and c = 4.077(2) Å. No systematic extinction has been observed, which is consistent with the *P6/mmm* space group adopted by Gd_2Fe_{17} annealed at 900°C (8). A total of 2738 reflections have been collected in the reciprocal

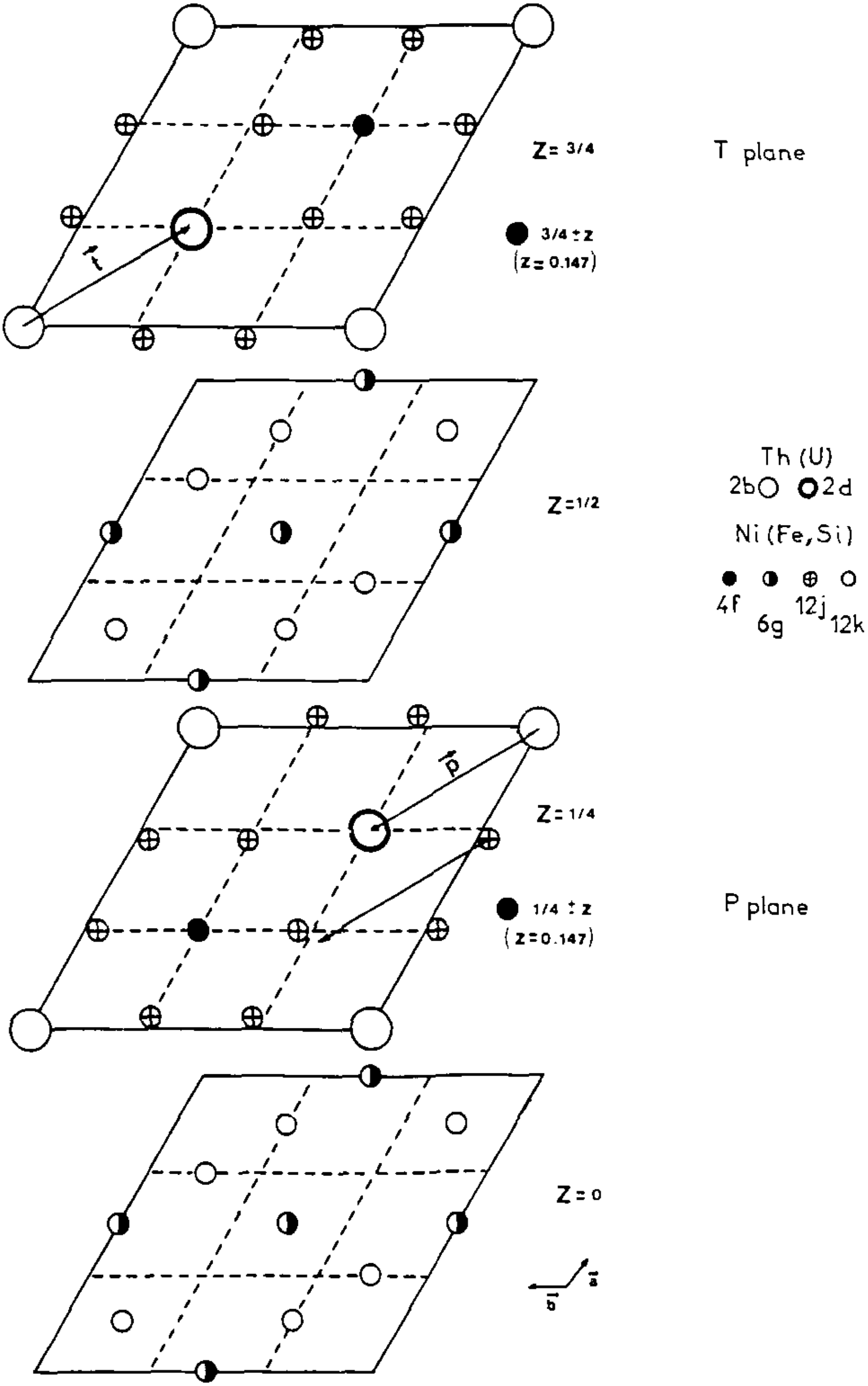

FIG. 2. Schematic representation along the c axis of the Th_2Ni_{17}-type structure.

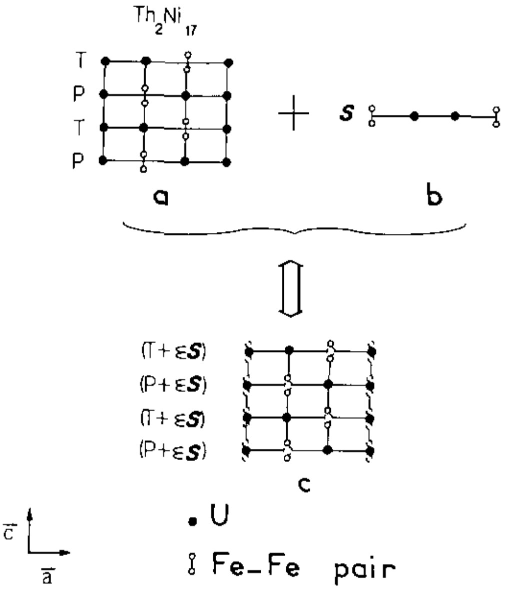

FIG. 3. Schematic representation of the Th_2Ni_{17}-type (a), the S plane (b), and the $U_2Fe_{13.3}Si_{3.7}$-type (c).

space $-9 \leq h \leq 9$, $-9 \leq k \leq 9$, and $-8 \leq l \leq 8$, yielding 171 unique reflections ($R_{INT} = 0.116$).

The structure refinement, made using a model deriving from the Gd_2Fe_{17}-type structure, leads to a final R value of 0.0253. The corresponding atomic positions are shown in Table III. For this compound, the U atom and the Fe1–Fe1 pair, which are randomly distributed, lead to the displacement of Fe2 or Si1 atoms located in the 6l site with an occupancy value of 33.3%. We note also that silicon cannot replace iron in its "dumbbell" site due to the short Fe1–Fe1 distance (2.420 Å) as already observed for $U_2Fe_{13.3}Si_{3.7}$. Here silicon is located in two kinds of planes perpendicular to the c axis; one of these planes also contains uranium atoms. This structural model proposed for $U_2Fe_{12.8}Si_{4.2}$ cannot explain the diffuse peaks occuring in the X-ray powder pattern (Fig. 1e). These extra lines could be due to a Th_2Zn_{17} arrangement for a small part of

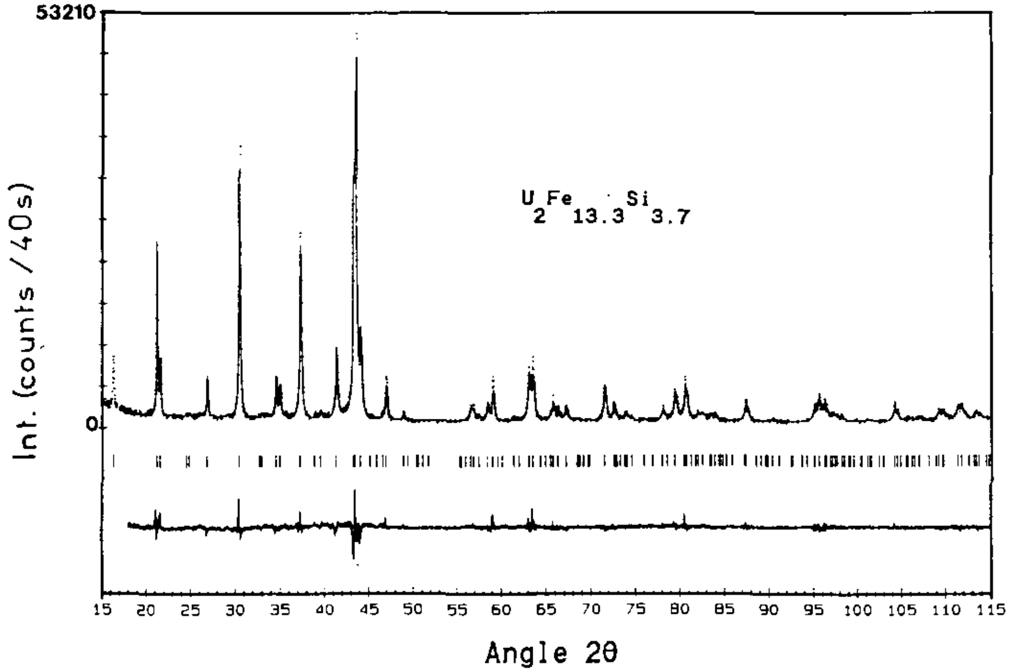

FIG. 4. Rietveld refinement plot of $U_2Fe_{13.3}Si_{3.7}$ silicide. The experimental data are shown by dots and the calculated fit by fulllines. The locations of reflections are indicated by small vertical bars.

TABLE III

ATOMIC COORDINATES, ISOTROPIC TEMPERATURE FACTORS, AND OCCUPANCY FOR $U_2Fe_{12.8}Si_{4.2}$ (*P6/mmm* SPACE GROUP)

Atom	Site	Position parameters				Occupancy	
		x	y	z	$B_{eq.}$ (Å)^2	No. of atoms	%
U	1a	0	0	0	0.85	0.667	66.7
Fe1	2e	0	0	0.2968(9)	0.56(6)	0.667	33.3
Fe2	6*l*	0.2957(3)	0.5914(7)	0	0.97(8)	1.383	23.0
Si1	6*l*	0.2957(3)	0.5914(7)	0	0.97(8)	0.617	10.3
Fe3	3g	$\frac{1}{2}$	0	$\frac{1}{2}$	1.20(3)	2.218	73.9
Si2	3g	$\frac{1}{2}$	0	$\frac{1}{2}$	1.20(3)	0.782	26.1

the sample as suggested by our preliminary electron microscopy study.

An increase of the silicon content in the $U_2Fe_{17-y}Si_y$ plays an important role in the order of the substitutions occurring between the uranium atoms and the iron–iron pairs. For $y = 3.7$ these substitutions are partially ordered, whereas they are statistically distributed for $y = 4.2$. This observation involves a structural transition from a derivative Th_2Ni_{17}-type structure to a derivative Gd_2Fe_{17} one.

Figure 5 shows the composition dependence of the unit cell parameters for the $U_2Fe_{17-y}Si_y$ compounds. For the sake of consistency, all the parameters are given for the hexagonal unit cell with Th_2Ni_{17}-type. When y increases, the c parameter decreases in the overall composition range, whereas the a parameter increases up to $y = 4$ and then remains practically constant. The c/a ratio decreases as y increases, showing that the unit cell dependence vs silicon content is strongly anisotropic (Table I). This result can be explained by the larger size of the silicon atoms which preferentially occupy the hexagonal basal plane, thus involving an expansion of the a parameter.

(*b*) *$U_2Co_{15}Si_2$*. The X-ray powder pattern of this ternary silicide is indexed on the basis of an hexagonal unit cell with $a = 8.2162(3)$ Å and $c = 8.1423(4)$ Å. This pattern has been analyzed by means of the Rietveld profile refinement technique in the Th_2Ni_{17}-type structure (Fig. 6). Atomic positions and occupancy values, given in Table IV, have been obtained using plausible values of the thermal factor B_{iso}, fixed for all atoms, by analogy to those determined for $UCo_{10}Si_2$ (*3*). In these conditions, the reliability factor R_I was 0.0838. For this compound, we have

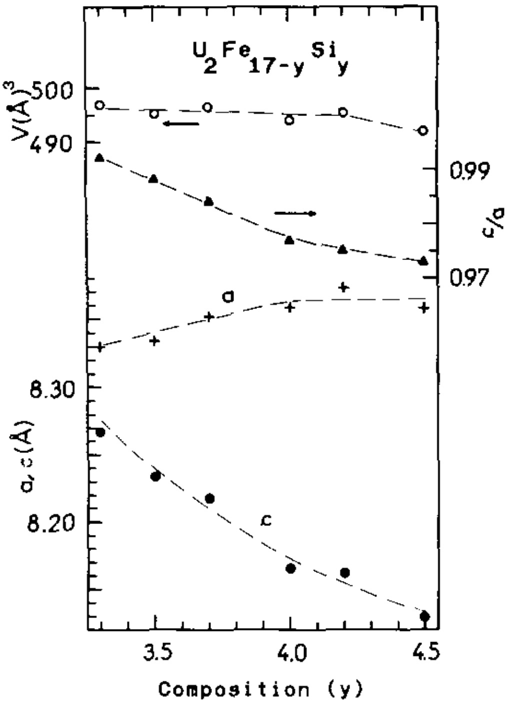

FIG. 5. Composition dependence of the unit cell parameters and volume of $U_2Fe_{17-y}Si_y$ silicides.

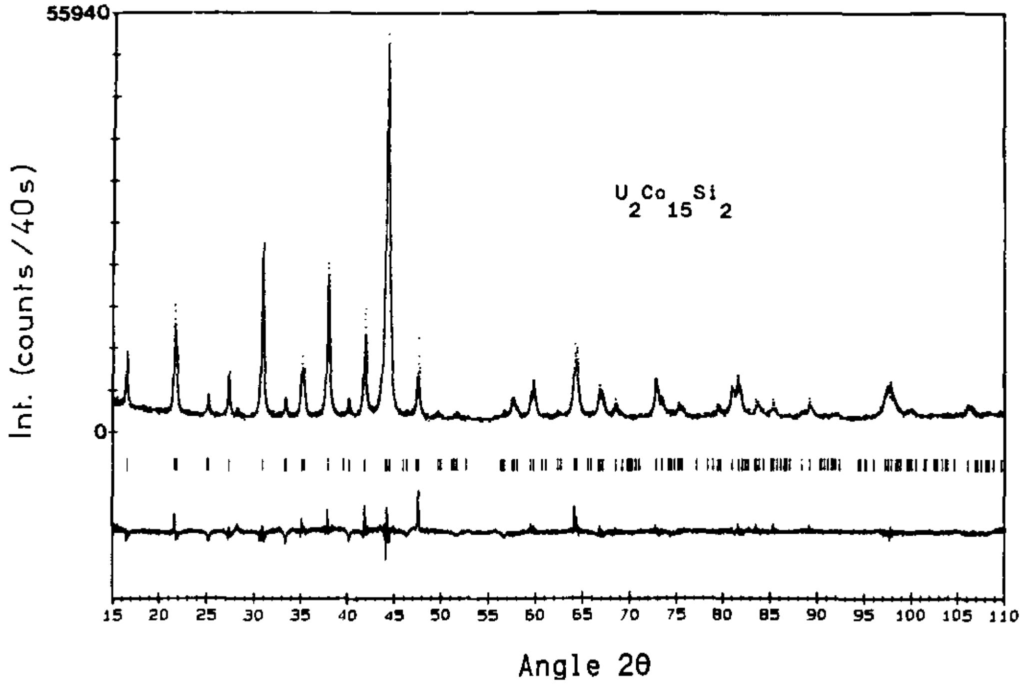

FIG. 6. Rietveld refinement plot of $U_2Co_{15}Si_2$.

also proposed to introduce some S planes as for $U_2Fe_{13.3}Si_{3.7}$. In this refinement the R_I factor, which drops off to 0.066, corresponds to $\varepsilon = 4.5\%$, characterizing the partial replacement of P or T planes by S planes. This result indicates that the structure of the $U_2Co_{15}Si_2$ compound is more ordered than that determined for $U_2Fe_{13.3}Si_{3.7}$ and therefore close to the ideal Th_2Ni_{17}-type structure. A similar comment has been made concerning Ho_2Fe_{17} and Ho_2Co_{17} (*10*).

Conclusion

We have shown that it is possible to stabilize new $U_2Fe_{17-y}Si_y$ ($3.3 \leq y \leq 4.5$) and

TABLE IV

REFINED STRUCTURAL PARAMETERS USING X-RAY POWDER DATA FOR $U_2Co_{15}Si_2$ (*P*6_3/*mmc* SPACE GROUP)

		Position parameters				Occupancy	
Atom	Site	x	y	z	$B_{eq.}$ (Å)^2	No. of atoms	%
U1	2b	0	0	$\frac{1}{4}$	0.2	2	100
U2	2d	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{4}$	0.2	2	100
Co1	4f	$\frac{1}{3}$	$\frac{2}{3}$	0.1034(7)	0.6	4	100
Co2	6g	$\frac{1}{2}$	0	0	0.6	3.8(1)	63.3
Si1	6g	$\frac{1}{2}$	0	0	0.6	2.2(1)	36.7
Co3	12j	0.0338(5)	0.6753(8)	$\frac{1}{4}$	0.6	12	100
Co4	12k	0.1642(7)	0.3284(7)	−0.0183(4)	0.6	10.2(1)	85.0
Si2	12k	0.1642(7)	0.3284(7)	−0.0183(4)	0.6	1.8(1)	15.0

$U_2Co_{15}Si_2$ compounds having a thermal stability dependent on the constituting transition element. Their crystal structure, which is derivative to the Th_2Ni_{17}-type structure, show some disordered substitutions between the uranium atoms and the iron–iron or cobalt–cobalt "dumbbell" sites. Particularly in the $U_2Fe_{17-y}Si_y$ system, the increase of the silicon content leads to an increase of the disordered substitutions, which is attended by a decrease of ferromagnetic properties: the Curie temperature T_C decreases linearly with rising y ($T = 525$ K for $y = 3.3$ and $T_C = 430$ K for $y = 4.5$) (*13*). On the other hand, this study has shown that silicon atoms never substitute for transition elements in the "dumbbell" sites.

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