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# New orthorhombic phase in U–Fe–Al–Si system

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ABSTRACT

A new quaternary phase with the approximate composition U–18.6 at%Fe–29.2 at%Al–32.6 at%Si was observed in U–Fe–Al–Si system. The crystal structure of this phase was investigated by electron diffraction and X-ray powder diffraction techniques. It has an orthorhombic unit cell with lattice parameters $a = 12.241$ Å, $b = 18.362$ Å and $c = 4.066$ Å and can be described by the *Immm* space group.



## 1. Introduction

Ternary aluminides in the Al-rich region of the U–Fe–Al system have been extensively investigated due to their interesting magnetic properties. Substantial part of the studies was focused on structural characterization of iron containing $UFe_xAl_{12-x}$ compounds [1–4] that exist in wide homogeneity range ($3 \le x \le 6$). They crystallize into a tetragonal structure of $ThMn_{12}$ type [5] described by the *I*4/*mmm* space group.

Ternary uranium silicides containing iron, $UFe_{12-x}Si_x$ ($1 \le x \le 3$), are related to another class of actinide based magnetic materials. Their typical representative, the $UFe_{10}Si_2$ compound, is also tetragonal and belongs to $ThMn_{12}$ structural type [6,7].

Systematical studies of Fe containing ternary uranium intermetallics with the $ThMn_{12}$ type structure have shown that their magnetic behavior is determined by contribution of different iron sublattices to the molecular magnetic moment and this, in its turn, depends on the concentration of the iron and on its distribution between different atomic sites in the unit cell [8–10]. These conclusions have aroused interest to quaternary compounds formed in U–Fe–Al–Si system in which joint presence of Al and Si should cause changes in occupation of different sublattices by iron atoms and, therefore, may influence magnetic behavior of material.

Although various review articles describing preparation of quaternary aluminum silicides have already been published [11], the reports on structure of quaternary aluminum silicides formed in U–Fe–Al–Si system are relatively scarce. Some information on $UFe_9AlSi_2$ compound has been reported in [12] while the results of structural investigation of two other quaternary phases, $UFe_7Al_3Si_2$ and $UFe_8Al_2Si_2$, were published in [13].

In the present work, we report on structural characterization of a new quaternary phase observed in the U–Fe–Al–Si system. This paper presents our results on characterization the symmetry and the unit cell parameters of the new compound.

## 2. Experimental

High purity uranium (99.99%), iron (99.97%), aluminum (99.999%) and silicon (99.9999%) were used to prepare U–14.8 wt% Fe–10.8 wt% Al–11.2 wt% Si alloy by arc melting in pure argon atmosphere. For homogeneity, the samples were re-melted several times and finally quenched by submerging into cold water. As-cast samples were investigated by XRD, SEM and TEM techniques.

Metallographic samples were prepared by conventional methods. The microstructure and the compositional profiles were analysed in scanning electron microscope JSM-5600 equipped with the Noran energy dispersive spectrometer (EDS).

Powder XRD pattern was recorded on a Philips PW3720 diffractometer equipped with a graphite monochromator for Cu-$K_\alpha$ radiation. The measurements were performed within $2\theta$ range from 5° to 100° at $2\theta$-step size of 0.02° with 18 s/step rate.

Specimens for TEM observations and micro-beam diffraction analysis were cut from a bulk material using a slow diamond disc cutter. They were mechanically polished to approximately 50 μm and then ion milled in *Gatan PIPS*™ machine. Transmission electron microscopy was carried out on a *JEOL FasTEM-2010* electron microscope equipped with *ThermoNORAN* EDS system for microprobe elemental analysis.

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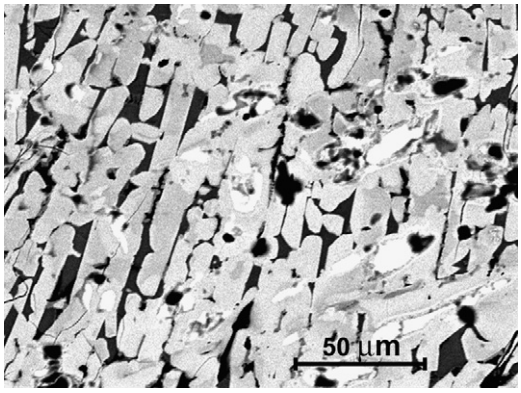


**Fig. 1.** Back-scattered SEM micrograph showing the microstructure of U–14.8 wt% Fe–10.8 wt% Al–11.2 wt% Si as-cast alloy. Uniformly distributed grey elongated grains of an unknown compound are surrounded by the $UFe_4(Al,Si)_8$ phase exhibiting black contrast. "White" phase is associated with the $U_2FeSi_3$ structure.

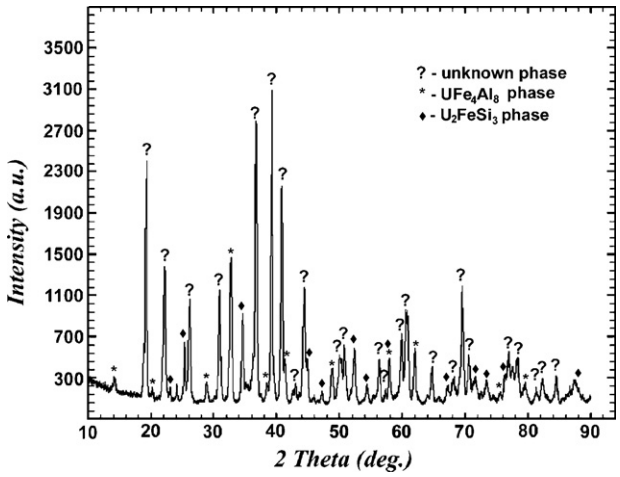


**Fig. 2.** X-ray powder diffractogram taken from U–14.8 wt% Fe–10.8 wt% Al–11.2 wt% Si as-cast alloy. Non-identified peaks are ascribed to the unknown new phase.

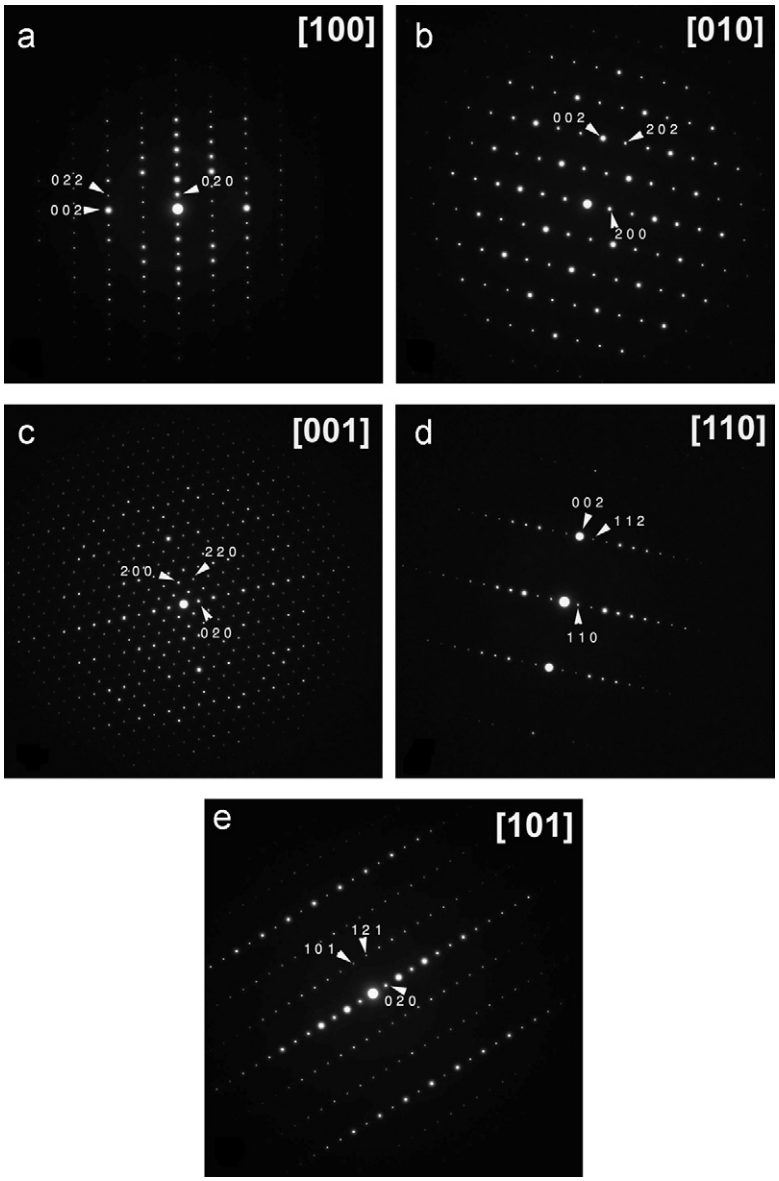


**Fig. 3.** Indexed selected area electron diffraction patterns taken from the new orthorhombic phase with zone axis parallel to (a) [1 0 0], (b) [0 1 0], (c) [0 0 1], (d) [1 1 0] and (e) [1 0 1] directions.

"Spinning Star" beam precession device developed by NanoMEGAS [14] was used to apply Precession Electron Diffraction technique [15] for determining the space group of the structure by analysis of the symmetry of zero- and high-order Laue zones. Precession semi-angles used for experiments were in the range of 1.5–2.0°.

## 3. Results and discussion

SEM micrograph (Fig. 1) taken with backscattered electrons shows the microstructure of the as-cast alloy. It mainly consists of grey elongated grains, which are separated with thin layers of another phase exhibiting black contrast. The third compound present in the alloy appears in the micrograph as bright white islands. Using the EDS compositional analysis the "black" and "white" phases were easily identified as $UFe_4(Al,Si)_8$ and $U_2FeSi_3$, respectively. The average composition of the grey phase was U–18.6 at% Fe–29.2 at% Al–32.6 at% Si; this phase could not be ascribed to any compound known in the literature.

X-ray diffraction pattern (Fig. 2) taken from the powder prepared from the as-cast alloy has confirmed the presence of $UFe_4(Al,Si)_8$ and $U_2FeSi_3$ phases in the alloy, although, most of the peaks observed in the diffractogram were not identified and were associated with the unknown structure. The reflections related to the $UFe_4(Al, Si)_8$ were indexed on the basis of the tetragonal unit cell $a = 8.736$ Å and $c = 5.030$ Å ($I4/mmm$) [4], and the reflections ascribed to $U_2FeSi_3$ phase were indexed in terms of the hexagonal unit cell ($P6/mmm$) $a = 4.004$ Å and $c = 3.864$ Å [16].

To determine the unit cell dimensions of the unknown phase a number of selected area electron diffraction (SAD) patterns were taken in TEM. Among them three patterns with the highest symmetry were ascribed to [1 0 0], [0 1 0] and [0 0 1] orientations of the crystal lattice (see Fig. 3a–c) and indexed in terms of the orthorhombic unit cell with the lattice parameters $a = 12.24$ Å, $b = 18.36$ Å and $c = 4.07$ Å, within an accuracy of approximately ±0.04 Å. On the basis of these parameters the rest of the SAD

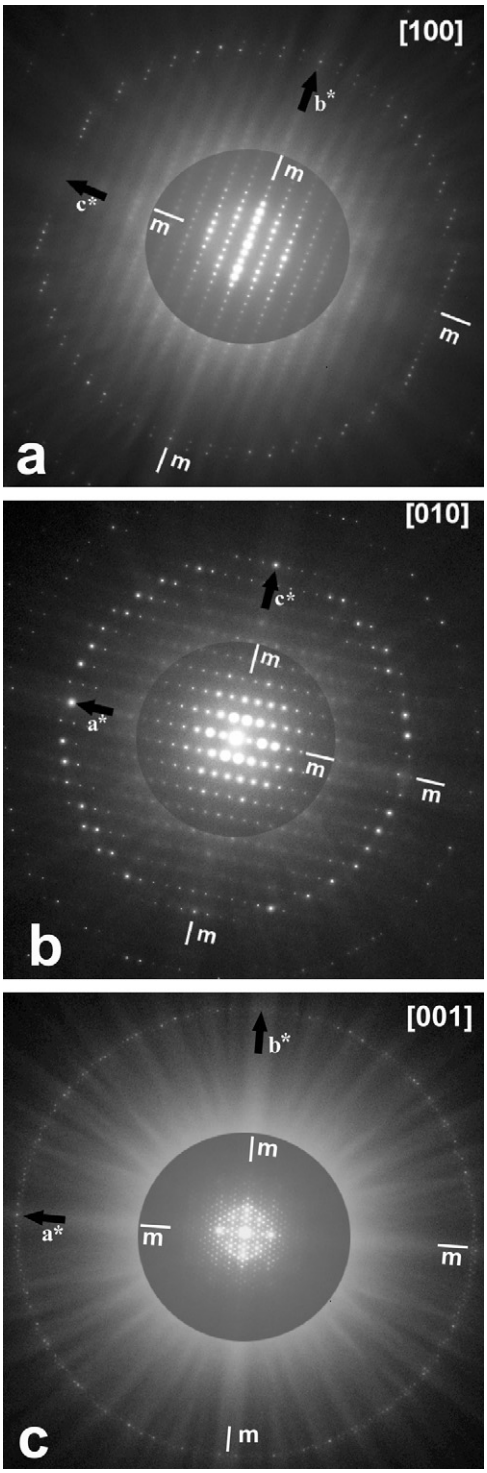


**Fig. 4.** Electron microdiffraction patterns from the new phase recorded along (a) [1 0 0], (b) [0 1 0] and (c) [0 0 1] directions.

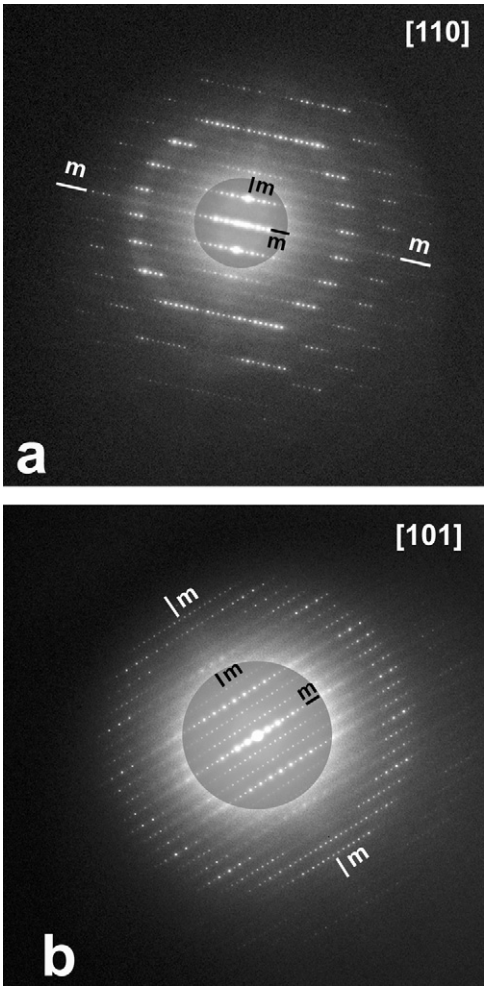


**Fig. 5.** Electron microdiffraction patterns obtained with beam precession technique. Zone axes correspond to (a) [1 1 0] and (b) [1 0 1] directions. In both patterns the symmetry of zero-order Laue zone is 2*mm*, while the whole-patterns show symmetry *m*.

patterns (see, for example, Fig. 3d and e for zone axes [1 1 0] and [1 0 1], respectively) and the peaks associated with the unknown phase in the X-ray diffractogram (Fig. 2) were also successfully indexed showing that the dimensions of the unit cell were correct.

A detailed analysis of the reflections related to the unknown phase that were observed both in SAD patterns and in X-ray diffractogram has shown that they obey the condition $h+k+l=2n$ thus indicating that the Bravais lattice is body centered.

The space group of the unknown phase was determined by the electron-microdiffraction technique through analysis of the symmetry of zero-order (ZOLZ) and first order (FOLZ) Laue zones [17]. The microdiffraction patterns recorded along [1 0 0], [0 1 0] and [0 0 1] directions are shown in Fig. 4a–c. It can be seen that ZOLZ and whole-pattern (WP) symmetry of [1 0 0], [0 1 0] and [0 0 1] patterns is 2*mm*, which is consistent with the point group *mmm* [17]. Precession Electron Diffractions taken along [1 0 1] and [1 1 0] zone axes (Fig. 5a and b) also show that the choice of *mmm* point group should be correct. The symmetry of zero-order Laue zone for both [1 0 1] and [1 1 0] patterns is 2*mm*, whilst the whole-pattern symmetry is *m*, which is consistent with *mmm* point group.

Typical shift between ZOLZ and the projected FOLZ reflection nets in [1 0 0] and [0 1 0] patterns demonstrates, again, that the Bravais lattice is body centered (*I*). Absence of periodicity differences between the ZOLZ and FOLZ indicates that the structure has no glide planes. Therefore, it can be deduced that the space group is *Immm* (no. 71).

It is worth noting that our identification of *mmm* point group was based on the assumption that our diffraction patterns possess "ideal" symmetry. Although the conclusions were made after careful analysis of many patterns obtained with precise alignment we were aware of the fact that subtle declination from the "ideal" symmetry may lead to wrong evaluation of the pattern symmetry. Actually, it was not a trivial task to distinguish between *m* and 2*mm* symmetries of [1 0 0] and [0 1 0] WP patterns. Should the symmetry of these patterns is *m* the correct choice of the point group must be *mm*2.

A reliable differentiation between point group *mmm* and *mm*2 was achieved from observation of convergent beam electron diffraction patterns (CBED) taken along the [1 1 0] and [0 1 0] zone axes. It can be seen that the [1 1 0] pattern (Fig. 6a) belongs to $2_R mm_R$ diffraction group showing *m* symmetry both for WP and for the bright-field disk, which is consistent with *mmm* point group in accordance with Buxton et al. [18]. If the point group *mm*2 were correct, we would have observed the pattern described by diffraction group $m_R$ with WP symmetry 1 (see Tables 2 and 4 in [18]).

The [0 1 0]CBED pattern (Fig. 6b) is also consistent with the *mmm* point group. This pattern corresponds to $2mm1_R$ diffraction group demonstrating 2*mm* symmetry both for WP and for the bright-field disk, whilst in the case of point group *mm*2 we would have observed $m1_R$ diffraction group described by WP symmetry *m* [18]. We are, therefore, convinced that the choice of *mmm* point group is correct.

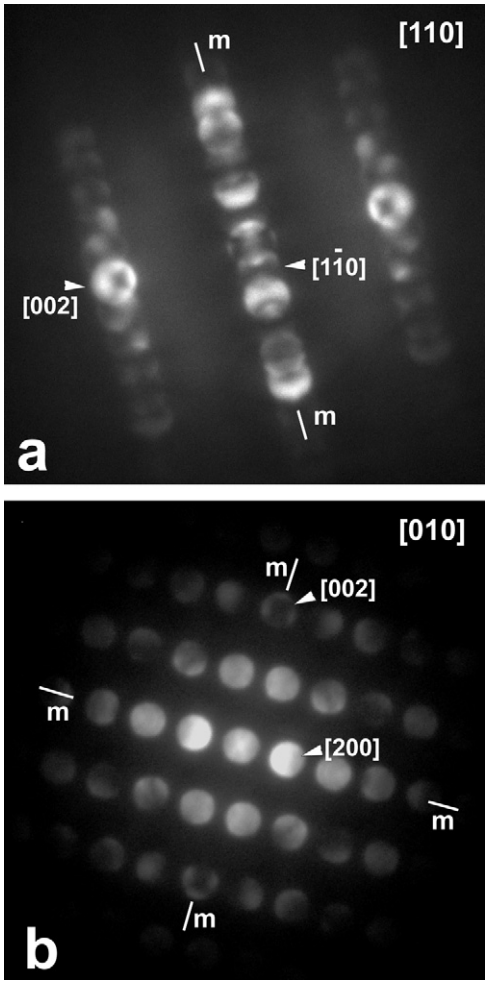


**Fig. 6.** CBED pattern taken with the beam aligned (a) along the [1 1 0] zone axis and (b) along the [0 1 0] zone axis. The pattern [1 1 0] belongs to $2_R mm_R$ diffraction group, showing *m* symmetry for the whole pattern, and symmetries *m* and 1 for the bright-field and general dark-field, respectively. The pattern [0 1 0] belongs to $2mm1_R$ diffraction group, showing 2*mm* symmetry both for the whole pattern and for bright-field disk.

## 4. Conclusions

A new quaternary intermetallic compound observed in the U–Fe–Al–Si system crystallizes in the orthorhombic structure with the unit cell parameters $a=12.241$ Å, $b=18.362$ Å and $c=4.066$ Å. Its symmetry can be described by the *Immm* space group. The composition of the new phase was specified as U–18.6 at% Fe–29.2 at%Al–32.6 at% Si. Further determination of its atomic structure is in progress.

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