

# Microscopic investigations of the ThMn<sub>12</sub>-type uranium ternaries

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## Abstract

The structure of the ThMn<sub>12</sub>-type uranium ternaries (UNi<sub>10</sub>Si<sub>2</sub>, UFe<sub>0.5</sub>Ni<sub>9.5</sub>Si<sub>2</sub> and UCo<sub>0.5</sub>Ni<sub>9.5</sub>Si<sub>2</sub>) was studied by high resolution transmission electron microscopy and electron diffraction. The general appearance of all the samples was similar, *i.e.* large individual crystals (a few micrometres) and aggregates of very fine, randomly oriented crystallites (10–30 nm) were observed. In addition, especially for the Fe-containing sample, another, distinct phase comprising very fine crystallites embedded in an amorphous matrix could be seen. The main constituent of all the samples was a tetragonal *I4/mmm* phase, isomorphous with ThMn<sub>12</sub>, with lattice parameters  $a=0.82$  nm and  $c=0.47$  nm. In addition, individual crystallites of a cubic phase ( $a=0.55$  nm), probably UO<sub>2</sub>, and another, unidentified phase exhibiting unusual contrast variations were found.

The ThMn<sub>12</sub>-type uranium compounds do not exist as binaries but they form ternaries with a high concentration of Fe, Co or Ni as the main component and with Si as a stabilizing element (for a review see ref. 1). Because of a complicated distribution of the transition metal atoms in the crystal lattice these compounds exhibit complex magnetic behaviour. UNi<sub>10</sub>Si<sub>2</sub> is paramagnetic with a reciprocal magnetic susceptibility following the modified Curie–Weiss law [2, 3] while the closely related compounds UFe<sub>10</sub>Si<sub>2</sub> and UCo<sub>10</sub>Si<sub>2</sub> are strongly ferromagnetic below 650 K and 550 K respectively [4, 5].

Our previous magnetic investigations of UFe<sub>0.5</sub>Ni<sub>9.5</sub>Si<sub>2</sub> have shown that its magnetic susceptibility does not exhibit Curie–Weiss behaviour and at about 630 K an anomaly in the temperature dependence of the magnetic susceptibility is observed. Another anomaly was detected at 32 K. Both phases below 630 and 32 K exhibit a ferromagnetic character [3] but <sup>57</sup>Fe Mössbauer effect examination revealed the splitting of the iron spectrum only below the low temperature transition [6]. It was suggested that the high temperature (HT) anomaly might result from precipitation of free Ni for which the Curie point is 630 K.

Preliminary results obtained in our laboratory for the similar UCo<sub>0.5</sub>Ni<sub>9.5</sub>Si<sub>2</sub> compound show that the temperature dependence of the magnetic susceptibility demonstrates only one anomaly but also at about 630 K. This last observation also suggests the free Ni as a reason for the HT anomaly. To elucidate the possibility

of the precipitation of micrograins of the Ni both in solid solutions and generally in a structure of UNi<sub>10</sub>Si<sub>2</sub> and its derivatives, we report on the results of examination of these materials by high resolution transmission electron microscopy (TEM) and electron diffraction methods.

The samples were prepared as described previously [2, 3]. The specimens for TEM were obtained by grinding a piece of an alloy in an agate mortar, dispersing it ultrasonically in methanol and placing a droplet of the suspension on a copper microscope grid covered with a carbon film. The grids were then examined in a Philips CM20 electron microscope equipped with a Super-Twin objective lens ( $C_s = 1.2$  mm), where both high resolution images and electron diffraction patterns were observed at 200 kV.

The overall morphology of all three samples studied by TEM (UNi<sub>10</sub>Si<sub>2</sub>, UFe<sub>0.5</sub>Ni<sub>9.5</sub>Si<sub>2</sub> and UCo<sub>0.5</sub>Ni<sub>9.5</sub>Si<sub>2</sub>) was similar. In each case the main constituents were aggregates of randomly oriented fine crystallites with sizes of 10–30 nm, but in addition also large individual crystals (a few micrometres) and very fine crystallites embedded in an amorphous matrix were observed as minor phases.

In Fig. 1 an electron micrograph of a typical fragment of UFe<sub>0.5</sub>Ni<sub>9.5</sub>Si<sub>2</sub> sample is shown together with the corresponding selected area diffraction (SAD) pattern. The scale bar on Fig. 1 shows the magnification applied. Thanks to the high resolution imaging used, individual crystallites can be distinguished as areas of parallel lattice fringes. The SAD pattern shown in Fig. 1 contains rings, which may be indexed in the tetragonal *I4/mmm*

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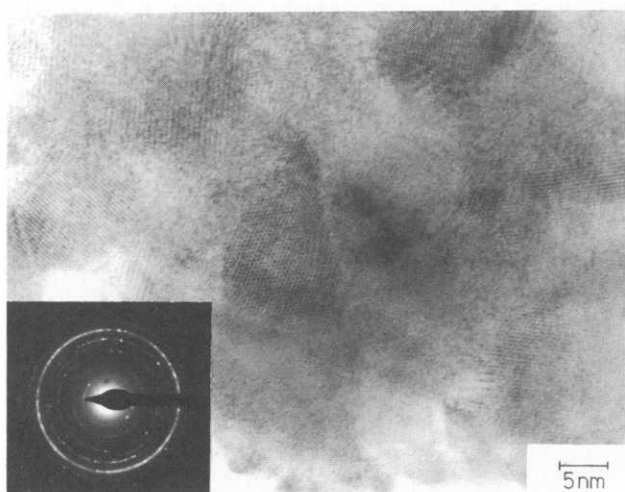


Fig. 1. Electron micrograph and SAD pattern of typical aggregate of small crystallites of  $\text{UFe}_{0.5}\text{Ni}_{9.5}\text{Si}_2$ . The crystallite in the centre is oriented with the [010] axis parallel to the electron beam.

structure with  $a = 0.82$  nm and  $c = 0.47$  nm. Both  $d$  values and intensities of the lines agree well with X-ray diffraction data, showing that the sample is isomorphous with  $\text{ThMn}_{12}$  [1]. SAD patterns and electron micrographs for typical fragments of the remaining samples were similar and are not shown here.

In the centre of Fig. 1 a crystallite exhibiting a regular array of dark spots is visible. Distances (0.47 and 0.82 nm) and angles ( $61^\circ$  and  $90^\circ$ ) between the spots suggest that they can represent columns of U atoms occupying the 2(a) sites in the  $\text{ThMn}_{12}$ -type structure oriented in such a way that the primary electron beam is parallel to the [010] crystal axis [1].

In Fig. 2 high resolution images and SAD patterns of two different, large crystals (a few micrometres) found in a  $\text{UCo}_{0.5}\text{Ni}_{9.5}\text{Si}_2$  sample are shown. The diffraction pattern in Fig. 2(a) contains strong reflections which form a square lattice with a period of 0.41 nm suggesting a [001]-oriented  $I4/mmm$  structure (the reflections could be indexed as (200), (020), (220) etc.). There is a problem, however, since instead of quite strong (110), (130) etc. reflections that should occur in such a case there are additional weaker reflections, (100), (120), (140) etc., normally forbidden in the  $\text{ThMn}_{12}$ -type structure. We believe therefore that the observed crystal exhibits a crystal structure that is a modification of the basic structure. The SAD pattern of a crystal shown in Fig. 2(b) (the closest-lying spots represent  $d$  values of 0.58, 0.49 and 0.32 nm) could not be indexed in the  $\text{ThMn}_{12}$ -type structure and we could not ascribe them to any known compound that could possibly be formed in this system. Interesting features observed in Fig. 2(b) are “microdomains” of different contrast having rod-like shapes and oriented parallel to certain crystal directions. The widths of the

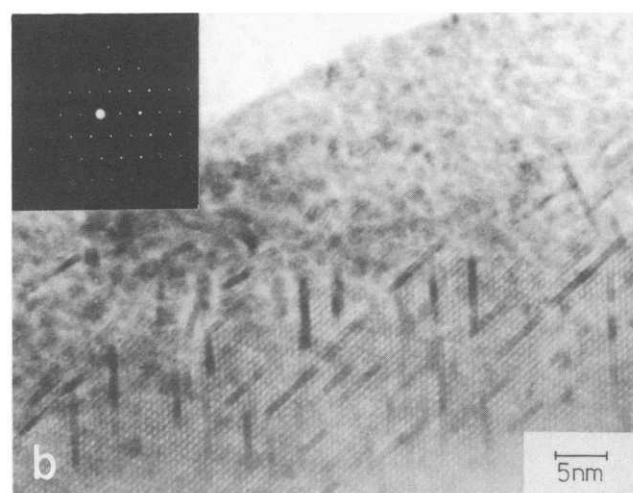
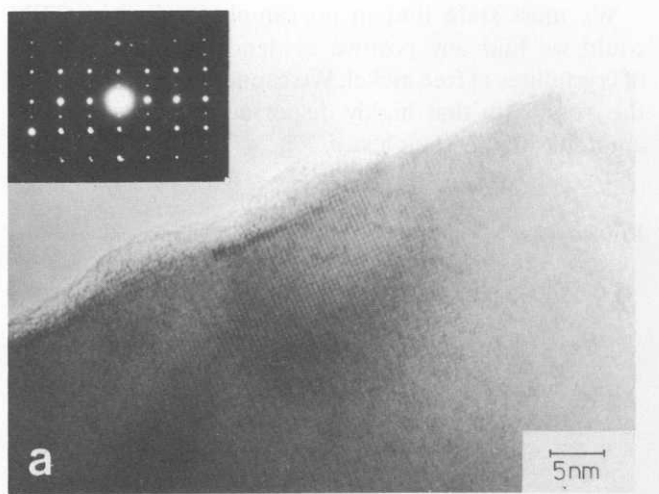


Fig. 2. High resolution images and SAD patterns of large crystals found in the  $\text{UCo}_{0.5}\text{Ni}_{9.5}\text{Si}_2$  sample: (a) modified  $I4/mmm$  phase; (b) unknown phase with “microdomains”.

“microdomains” fit exactly the interplanar distances in the lattice (about 0.5 nm) indicating that in fact they may have a flake-like shape (in Fig. 2(b) we see only a cross-section or more strictly a projection of the lattice). The origin of the observed inhomogeneities in the image contrast is unclear but they could possibly be caused by inhomogeneities in the distribution of either electric or magnetic field. It should be noted that in TEM a specimen is placed during observation in quite a strong external magnetic field generated by the objective lens.

In addition to the crystalline phases described above we found occasionally in each sample large crystals of a cubic substance with  $a = 0.55$  nm (probably  $\text{UO}_2$ ) and (particularly in  $\text{UFe}_{0.5}\text{Ni}_{9.5}\text{Si}_2$ ) a certain amount of disordered material in which very fine (a few nanometres) particles of another phase were embedded. Because of the lack of any well-defined reflections no identification of the phases was possible.

We must state that in no sample studied by TEM could we find any positive evidence for the presence of crystallites of free nickel. We cannot exclude, however, the possibility that highly dispersed Ni exists in small amounts in the samples.

## References

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