The Crystal Structures of $U_2Cu_3Al$ and $UCuAl_3$, and their Relationship with Some Other Phases in the System $U-Cu-Al$

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X-ray investigations of a great number of samples along the specifically chosen tie-lines in the isothermal sections of the system $U-Cu-Al$ (800 °C) indicated the existence of two new ordered ternary phases, i.e. $U_2CuAl$ and $UCuAl_3$.

The first one is hexagonal (8. G. P6/ammc, MgZn$_2$-type), with $a = 5.065 \pm 0.005 \text{ Å}$, $c = 8.307 \pm 0.005 \text{ Å}$ and $c/a = 1.640$. The ordered atomic arrangement of all atoms, as confirmed by trial and error method is consistent with a rather uncommon superstructure of the MgZn$_2$-type.

$UCuAl_3$ is tetragonal, $a = 3.857 \pm 0.005 \text{ Å}$, $c = 8.736 \pm 0.005 \text{ Å}$, $c/a = 2.265$, probable space group is I4/mmm, and represents an ordered ternary structure variant of the TiAl$_3$ type.

The crystal structures of these two new phases were correlated, in terms of stacking sequences, with those which were identified in this system previously.

Introduction

In our earlier paper [1] describing the investigations on substitution of copper in UCu$_5$ (cubic variant of AB$_5$-structure type) with aluminium, it was demonstrated that the addition of a small amount of the third component (Al), causes the cubic UCu$_5$ to transform into a hexagonal Friauf-Laves structure of the MgZn$_2$-type. Further addition of aluminium results in a structure of the CaCu$_5$-type. It ought to be pointed out that all phases lying on the tie-line UCu$_5$-xAl$_x$ have the structure of some of Friauf-Laves or closely related AB$_5$-type.

As the system $U-Cu-Al$ was not studied yet we felt that some other specifically chosen tie-lines in the isothermal section (especially those with possible ternary superstructure of Friauf-Laves phases) would be worth investigating. Thus the tie-lines UCu$_5$-$UAl_3$ and UCu$_3$-$UAl_3$ were chosen.

Experimental

Materials and Methods

The following metals were used: Copper powder (B. D. H., reagent grade), aluminium powder (Koch-Light Laboratories Ltd., 99%) and uranium filings (99.93%, obtained from Institute "Boris Kidric", Vinča, Yugoslavia) preliminary cleaned in a mixture of conc. nitric acid and ethanol (1:1) to remove surface oxide.

Samples of the general formula $UCu_2-xAl_x$ and $UCu_2-xAl_3$ were prepared by arc melting appropriate quantities of elements in an argon atmosphere using a titanium button acting as a getter. The samples were annealed at 800 °C for 700 h in evacuated quartz glass vials and slowly cooled (50 °C/day).

X-ray powder diffraction patterns were taken on a Philips diffractometer PW 1050, using nickel filtered CuK radiation. X-ray diffraction line intensities were calculated on a Univac 1110 computer, taking into account the structure factor, the Lorentz polarization factor and the multiplicities. Single phase patterns were indexed graphically using Bunn’s charts and crystal structures were determined by trial and error method.

Results and Discussion

The results of X-ray examinations indicated the existence of two new ternary phases of the composition $U_2CuAl$ and $UCuAl_3$, respectively. The first one along the tie-line UCu$_2$-$UAl_3$ and the second one on UAl$_3$-$UCu_3$.

The unit cell of $U_2CuAl$ is hexagonal with $a = 5.065 \pm 0.005 \text{ Å}$, $c = 5.065 \pm 0.005 \text{ Å}$ and $c/a = 1.640$. Comparison between calculated and theoretically determined density values showed the best agreement if unit cell contains two formula units ($\rho_x = 12.48 \text{ g/cm}^3$ and $\rho_e = 12.19 \text{ g/cm}^3$).

On the basis of the clear resemblance of X-ray patterns to those of MgZn$_2$, as well as taking into account the number of atoms per unit cell the MgZn$_2$-type of structure was postulated. Observed
and calculated intensity values are in best agreement if the following atomic positions are assumed:

4 U in 4(f) 1/3, 2/3, z, 2/3, 1/3, 2 + z, 2/3, 1/3, z, 1/3, 2/3, 1/2 — z.
2 Al in 2(a) 0, 0, 0, 0, 0, 1/2.
6 Cu in 6(h) x, 2x, 1/4, 2z, z, 1/4, x, z, 1/4, x, 2x, 3/4, 2x, x, 3/4, z, x, 3/4.

The variable parameters were found to assume the following values: \( \sigma = 0.025 \) and \( x = 0.840 \).

Fig. 1 illustrates the structure. The relevant diffraction data can be obtained from the authors. For comparison the calculated intensity values for statistical distribution of aluminium and copper atoms in positions 2(a) and 6(h) were considered. \( \sigma = 13.6 \) and 20.1\% respectively. A set of acceptable interatomic distances is thus obtained:

\[
\begin{align*}
\text{U} - \text{U} & \quad 2.939 \text{ Å} \\
\text{U} - \text{Al} & \quad 2.932 \text{ Å} \\
\text{U} - \text{Cu} & \quad 2.743 \text{ Å} \\
\text{Al} - \text{Cu} & \quad 2.507 \text{ Å} \\
\text{Cu} - \text{Cu} & \quad 2.431 \text{ Å}
\end{align*}
\]

Fig. 1. The crystal structure of \( \text{U}_2\text{Cu}_3\text{Al} \) (origin at 2/3, 1/3, 3/4, \( \text{MgZn}_2 \)-type).

Among many known ternary intermetallic compounds of \( \text{MgZn}_2 \)-type only few exhibit ordered atomic arrangement (superstructure), \( \text{e.g. Mg}_2\text{Cu}_3\text{Si}, \text{Nb}_2\text{Co}_3\text{Si} \) and \( \text{Mn}_2\text{Cu}_3\text{Ge} \) [2–4].

The useful superstructure lines to be mentioned would be 114 and 304. They should be extinct in the case of a statistical atomic arrangement in positions 2(a) and 6(h) providing that the variable parameters for these positions are ideal, \( \text{i.e. } x = 0.833 \) and \( z = 0.065 \). However, since in \( \text{U}_2\text{Cu}_3\text{Al} \) structure the variable parameters are significantly different from ideal values \( (x = 0.840 \) and \( z = 0.025 \)), the 114 and 304 reflections occur with statistical as well as with the ordered atomic arrangement.

The probable space group of the compound \( \text{UCuAl}_2 \) is I\( _4 \)/mmm, with \( \alpha = 3.857 \pm 0.005 \text{ Å}, c = 8.736 \pm 0.005 \text{ Å} \) and \( c/\alpha = 2.265 \). The analysis of extinct reflections and the number of formula units per unit cell (equaling two) as deduced from densities \( (\rho_x = 9.08 \text{ g/cm}^3, \rho_e = 8.79 \text{ g/cm}^3) \) led us to the \( \text{TiAl}_3 \)-type of structure. This was confirmed by the intensity calculations which were carried out for several assumed atomic arrangements within the unit cell. The best agreement was obtained for the following atomic coordinates:

\[
\begin{align*}
2 \text{ U} \text{ in } 2(a) & \quad 0, 0, 0, 1/2, 1/2, 1/2. \\
2 \text{ Cu} \text{ in } 2(b) & \quad 0, 0, 1/2, 1/2, 1/2, 0. \\
4 \text{ Al} \text{ in } 4(d) & \quad 1/2, 0, 3/4, 0, 1/2, 3/4, \\
& \quad 0, 1/2, 1/4, 1/2, 0, 1/4.
\end{align*}
\]

All interatomic distances in this structure are acceptable \( (R = 12.2\%) \):

\[
\begin{align*}
\text{U} – \text{Cu} & \quad 2.727 \text{ Å} \\
\text{U} – \text{Al} & \quad 2.913 \text{ Å} \\
\text{Cu} – \text{Al} & \quad 2.913 \text{ Å} \\
\text{Al} – \text{Al} & \quad 2.727 \text{ Å}
\end{align*}
\]

The structure of \( \text{UCuAl}_2 \) is best described as a superstructure derived from \( \text{UAI}_3 \) (\( \text{AuCu}_3 \)-type), by substituting certain aluminium atoms with copper in crystallographic positions 3(c), and doubling one of the cubic axes which thus becomes the tetragonal axis \( c \). The ideal \( c/\alpha \) ratio equals two, but in \( \text{UCuAl}_2 \) structure some deviation is observed. In

Fig. 2. The crystal structures of \( \text{UAI}_3 \) (\( \text{AuCu}_3 \)-type) and \( \text{UCuAl}_2 \) (\( \text{TiAl}_3 \)-type).

the structure of UAl₃ all layers with mixed atoms (U + Al) are in register, while in UCuAl₃ mixed layers (U + Cu) are displaced by a/2, a/2, 0 (parallel translation) (Fig. 2).

It may be interesting to make some structural correlations of the phases described here together with others in the same system reported elsewhere [1], and corresponding binary prototipes in terms of stacking sequences. It can be easily shown that all these phases have a common stacking sequence motive, i.e. as shown by Frank and Kasper [5], they are all based on kagomé nets (alternatively) interleaved with three triangular nets at different levels (except for CaCu₅).

On Figs. 3 a and 3 b, one can see a characteristic kagomé net and a projection of triangular nets for each particular structure. In hexagonal and cubic phases layers of atoms are parallel to (001) and/or (111) plane, respectively. It is apparent that copper atoms are gradually being substituted by aluminium atoms, or vice-versa, in kagomé nets only.

Fig. 3 a. Kagomé nets and projections of triangular nets in UCu₅, U₂Cu₅Al and UCu₅Al₁₅.

Fig. 3 b. Kagomé nets and projections of triangular nets in UAl₂ and U₂Cu₃Al.

Fig. 4 illustrates the well known transition from triangular ordering of uranium atoms in UAl₃, to rectangular ordering in UCuAl₂ (layers are parallel to (112) plane of the tetragonal unit cell).