Crystallographic study of new phases from the U–Zn–Al ternary system

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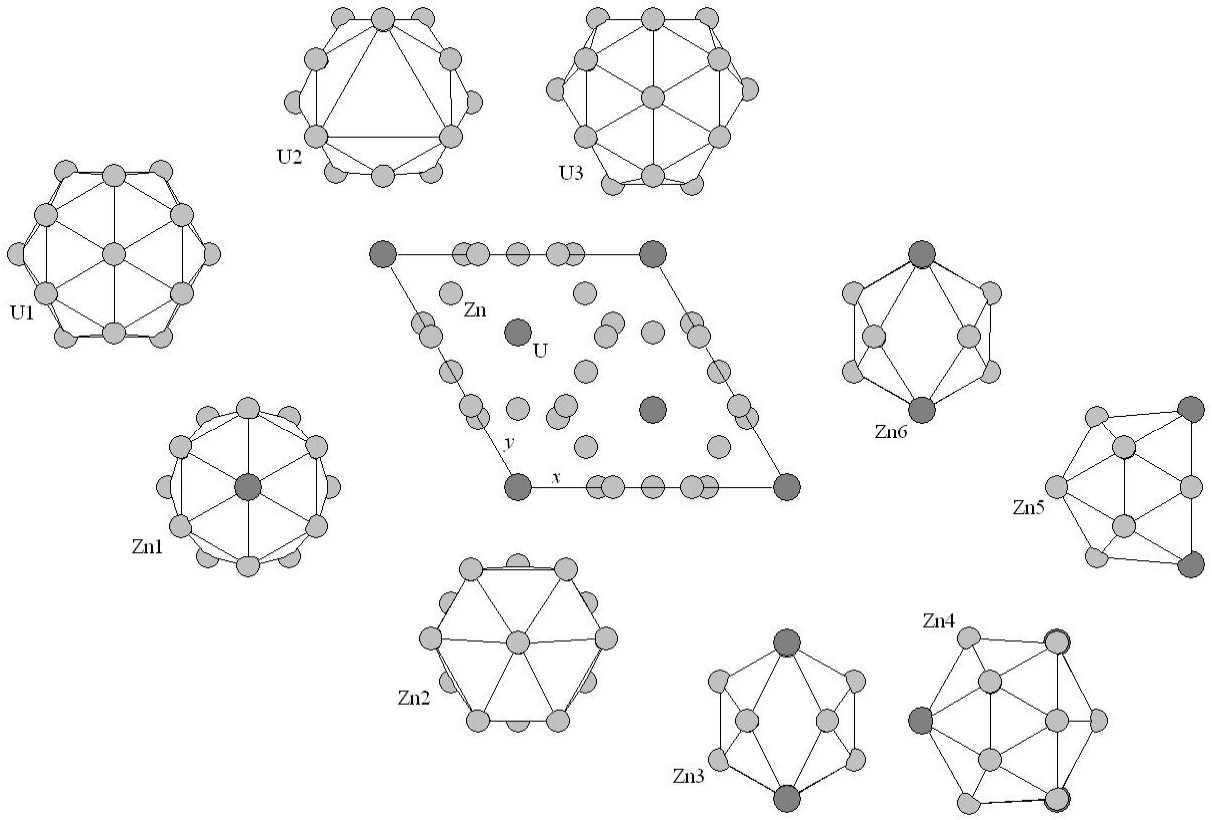
Uranium based intermetallic compounds have been intensively studied due to their unusual ground states and behaviours (as intermediate valence states, heavy fermion behaviours, unconventional superconductivity, etc.). The binary U–Zn system is characterised by the existence of two compounds, UZn_{12-x} (high–temperature form of $SmZn_{12}$) and U_2Zn_{17} (crystallizing in two polymorphic modifications, with Th_2Zn_{17} and Th_2Ni_{17} structure types, respectively), which show coexistence of magnetism and heavy fermion behaviour [1,2]. Albeit this, the study of U–Zn–X (X = p element) ternary systems is still scarce. This work is a part of our systematic investigation of uranium – d– and p–metal alloy systems and consists on the exploration of the U–Zn–Al phase diagram and identification of the ternary compounds and solubility ranges.

The samples were synthesized at 950ºC from the pure elements, inside quartz ampoules under vacuum. No reaction with the quartz ampoules was observed. The obtained products were characterized by using X–ray powder diffraction techniques. Needle–shape high quality crystals were selected from crushed samples with nominal $\sim U_{10}Zn_{60}Al_{30}$ composition and used in the X–ray diffraction measurements. The experiments were made at room temperature by using a four–circle Nonius CAD4 diffractometer with graphite monochromatized Mo Kα–radiation and a scintillation counter with pulse height discrimination. Scans were taken in the $\omega/2\theta$ mode. Empirical absorption corrections were applied on the basis of Ψ–scan data. The crystal structure was refined using Shelxl–97 [3] (full–matrix least–squares on F^2). The unit cell parameters were obtained by least–squares refinement of the 2θ values of 25 intense and well–centered reflections from various parts of the reciprocal space ($16°<2\theta<36°$).

The X–ray powder diffraction data of the as–prepared $\sim U_{10}Zn_{60}Al_{30}$ sample shows the presence of three phases: $Zn_{1-x}Al_x$ (Mg–type), binary UAl_3 ($AuCu_3$–type) and hexagonal phase $U_x(Zn_{1-y}Al_y)_z$, with cell dimensional: a = 9.047(1) Å, c = 8.858(1) Å, V = 627.9(1) Å^3. The cell dimensions fitting, from the 25 reflections and performed for several single crystals, gave always similar results: a ~9.03 Å, c ~8.82 Å, V ~622 Å^3. After testing various models for well–known structures of binary R–Zn and ternary R–Zn–X compounds (R = rare earth), our attention was stopped on the high–temperature form of $SmZn_{12}$ type structure (space group *P6/mmm*). In a first stage this structure type was adopted in the $U_x(Zn_{1-y}Al_y)_z$ structural refinement from the single crystal X–ray diffraction data and residuals R_1 = 0.0642, R_w = 0.1154 (405 F^2 values, 41 variables) were obtained. The composition of this hexagonal phase was also refined, being obtained $\sim U_{1.12}Zn_{9.51}Al_{1.71}$ (=$U_9Zn_{77}Al_{14}$). However, quite high residual factors still remain, which could indicate that the structure of the above mentioned phase was not exactly of the $SmZn_{12}$ type, but some derived from it. In a second step direct methods were used and the $U_x(Zn_{1-y}Al_y)_z$ crystal structure was determined and refined.



Projections of the $U_{1.12}Zn_{9.51}Al_{1.71}$ structure on the *xy* plane
and coordination polyhedra of the atoms.

Acknowledgments

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References

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