

## Single crystal investigation of the ht-U<sub>2</sub>Zn<sub>17</sub> binary compound

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**The high-temperature U<sub>2</sub>Zn<sub>17</sub> phase (U<sub>1.71(1)</sub>Zn<sub>17(1)</sub>) has been obtained from a sample of nominal composition 10U:90Zn (at.%), prepared by high-temperature (950°C) synthesis. Its crystal structure was determined from X-ray single crystal diffraction data: space group *P6<sub>3</sub>/mmc*, *a* = 9.0304(16) Å, *c* = 8.817(4) Å, *V* = 622.7(3) Å<sup>3</sup>, *R*<sub>1</sub> = 0.0391, *wR*<sub>2</sub> = 0.0830. The structure is closely related to the Th<sub>2</sub>Ni<sub>17</sub> and LuFe<sub>9,5</sub> structure types. The analysis of the interatomic distances indicates strong interactions between the Zn atoms.**

### Binary phase / Crystal structure / X-ray diffraction

#### Introduction

Uranium-based intermetallic compounds have been intensively studied due to their unusual ground states and behavior (intermediate valence states, heavy fermion behavior, unconventional superconductivity, etc.) [1,2]. The binary U–Zn system is characterized by the existence of two compounds, UZn<sub>12</sub>, with own structure type, and U<sub>2</sub>Zn<sub>17</sub>, crystallizing in two polymorphic modifications with Th<sub>2</sub>Zn<sub>17</sub> and Th<sub>2</sub>Ni<sub>17</sub> structure types at low (lt-U<sub>2</sub>Zn<sub>17</sub>) and high (ht-U<sub>2</sub>Zn<sub>17</sub>) temperature, respectively. Both compounds revealed small homogeneity ranges [3]. Single crystal investigations of the UZn<sub>12</sub> compound showed different partially disordered arrangements of the zinc atoms [4,5]. Structural parameters for the lt-U<sub>2</sub>Zn<sub>17</sub> phase, obtained from powder as well as single crystal X-ray diffraction data, pointed to the Th<sub>2</sub>Zn<sub>17</sub>-type structure for this phase [6,7]. Single crystal investigations of ht-U<sub>2</sub>Zn<sub>17</sub> have not been conducted; a superstructure model, based on the Th<sub>2</sub>Ni<sub>17</sub>-type structure, was proposed by the authors of [8] using powder X-ray diffraction data. The aim of this work was to clarify the real crystal structure of the ht-U<sub>2</sub>Zn<sub>17</sub> phase by performing single crystal X-ray diffraction studies.

#### Experimental

Metals with purities >99.95 wt.% (uranium ingots and zinc tear drops) were used as starting materials. A sample, with nominal composition 10U:90Zn (at.%), was synthesized by heating the elements at 950°C

inside quartz ampoules under vacuum for one hour, followed by fast air-quenching. Suitable block-like single crystals were selected from the crushed sample and used in the X-ray diffraction experiment.

Single crystal intensity data were collected at room temperature using a four-circle Enraf-Nonius Mach III diffractometer with graphite monochromatized Mo *K* $\alpha$ -radiation and a scintillation counter with pulse height discrimination. Scans were performed in the  $\omega/2\theta$  mode. An empirical absorption correction was applied on the basis of  $\psi$ -scan data. The structure was solved by direct methods using SIR97 [9], and refined using SHELXL-97 [10] available in the WinGX package [11]. The unit cell parameters were obtained by least-squares refinement of the  $2\theta$  values of 25 intense and well-centered reflections from various parts of the reciprocal space ( $15^\circ < 2\theta < 30^\circ$ ). Crystallographic and experimental details of the structure determination are listed in Table 1.

#### Results and discussion

The analysis of the data set showed systematic extinctions that were compatible with space groups *P6<sub>3</sub>/mmc*, *P6<sub>3</sub>mc* and *P-62c*. The centrosymmetric group was found to be correct during the structure refinement. Six atomic positions were obtained from the direct methods: the uranium atoms occupy the *2b* and *2c* sites, while the zinc atoms are situated in *4f*, *6g*, *12j*, and *12k* sites. At the next step of the refinement one more uranium position (*2d*) and two zinc–zinc pairs (*4e* and *4f*) were located from the difference electron density map.

**Table 1** Crystal data and experimental details for ht-U<sub>2</sub>Zn<sub>17</sub>.

Phase	ht-U <sub>2</sub> Zn <sub>17</sub>
Composition from refinement	U <sub>1.71(1)</sub> Zn <sub>17(1)</sub>
Relative molar mass	1504.93
Crystal system	Hexagonal
Space group	<i>P6<sub>3</sub>/mmc</i> (No. 194)
Pearson symbol	<i>hP37</i>
Unit cell dimensions	
<i>a</i>	9.0304(16) Å
<i>c</i>	8.817(4) Å
<i>V</i>	622.7(3) Å <sup>3</sup>
Formula units per cell	2
Calculated density	8.027 g/cm <sup>3</sup>
Crystal shape and color	Block, Silvery
Diffractometer	Enraf-Nonius Mach III
Radiation	Mo Kα ( $\lambda = 0.71073$ Å)
Monochromator	Graphite
Temperature	293(2) K
Absorption coefficient	53.727 mm <sup>-1</sup>
<i>F</i> (000)	1322
$\theta$ range for data collection	2.60° to 29.95°
Scan type	$\omega$ -2 $\theta$
Range in <i>hkl</i>	-12 → 12, -12 → 12, -12 → 12
Total no. reflections	6546
Independent reflection	374
Reflections with $I > 2\sigma(I)$	265
<i>R</i> <sub>eq</sub> , <i>R</i> <sub><math>\sigma</math></sub>	0.1509, 0.0401
Structure refinement	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	274/2/38
Goodness-of-fit on <i>F</i>	1.097
Final <i>R</i> indices <sup>a</sup>	<i>R</i> 1 = 0.0391, <i>wR</i> 2 = 0.0830
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0658, <i>wR</i> 2 = 0.0934
Weighting scheme <sup>b</sup>	<i>a</i> = 0.0395, <i>b</i> = 8.1273
Extinction coefficient	0.0013(3)
Largest diff. peak/hole	2.356/-1.791 e/Å <sup>3</sup>

$$^a R1 = \sum(|F_o| - |F_c|) / \sum|F_o|, wR2 = \{\sum w[(F_o^2 - F_c^2)^2] / \sum w[(F_o^2)^2]\}^{1/2};$$

$$^b w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP], \text{ where } P = (F_o^2 + 2F_c^2)/3.$$

The occupancy parameters were verified step-by-step. Full occupancy was observed only for the 6*g*, 12*j* and 12*k* sites. The isotropic displacement parameters of atoms for the sites with occupancy *G* less than 0.05 (Zn2 and U3) were fixed to 0.02 Å<sup>2</sup>, while the other atomic positions were refined in the isotropic (for *G* < 0.5: Zn1) or anisotropic mode (for *G* > 0.5: U1, U2, Zn3, Zn4, Zn5, and Zn6). The relatively large values of the anisotropic parameter *U*<sub>11</sub> for Zn5 and of *U*<sub>33</sub> for Zn6 pointed to a possible displacement of these atoms from the initial model. Thus these positions were split into two constrained ones, called Zn5A and Zn5B, and Zn6A and Zn6B, respectively, and refined with isotropic displacement parameters. The results of the refinement are presented in **Table 2**.

It can be noted that the final structural model of the ht-U<sub>2</sub>Zn<sub>17</sub> (U<sub>1.71</sub>Zn<sub>16.81</sub>) phase is closely related to the Th<sub>2</sub>Ni<sub>17</sub> and the disordered LuFe<sub>9.5</sub> (or Lu<sub>1.825</sub>Fe<sub>17.35</sub>) structure types [12]. Similar atomic

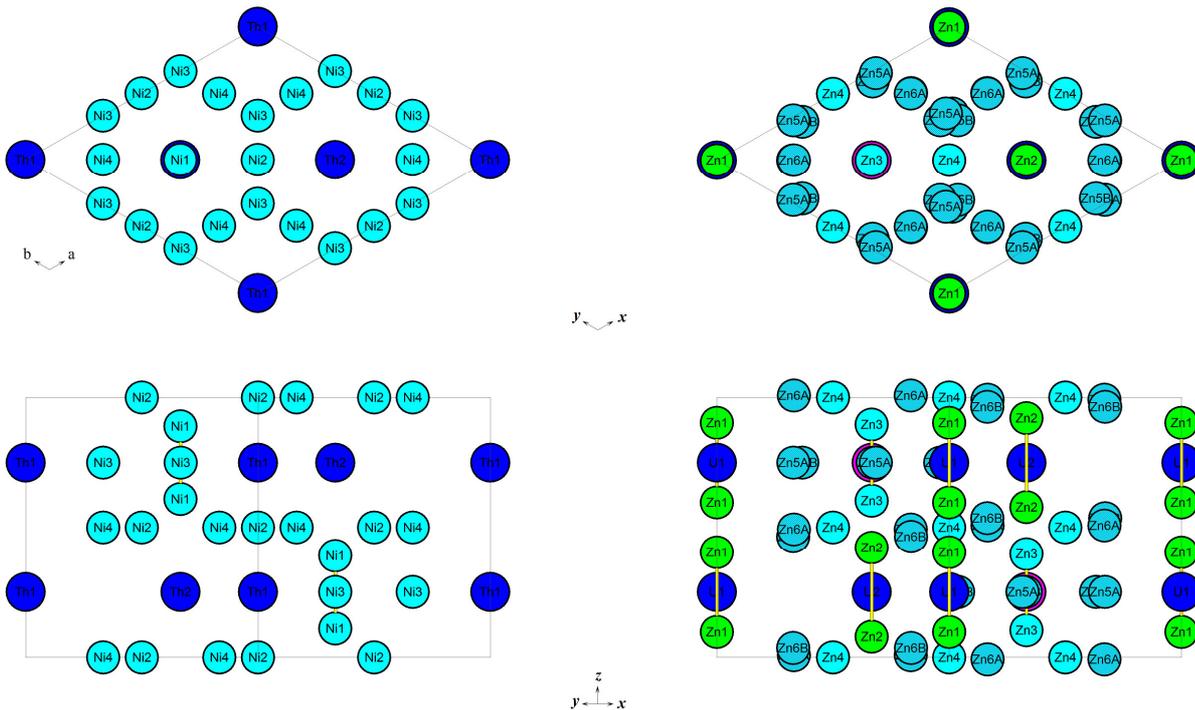
disorder among binary prototypes is also known for Ho<sub>2</sub>Co<sub>17</sub> (or Ho<sub>2.18</sub>Co<sub>15.56</sub>) and CeMg<sub>10.5</sub> (or Ce<sub>1.71</sub>Mg<sub>17.58</sub>). All these structures can be described as defect versions of the well-known Th<sub>2</sub>Ni<sub>17</sub> structure type [12]. The differences between Th<sub>2</sub>Ni<sub>17</sub> and U<sub>2</sub>Zn<sub>17</sub> are shown in **Fig. 1**. In U<sub>1.71</sub>Zn<sub>16.81</sub> the uranium atoms (U1, U2 and U3) are located in three Wyckoff positions (2*b*, 2*c* and 2*d*), and are partially replaced by Zn–Zn dumbbells (denoted as Zn1 in 4*e*, Zn2 in 4*f*, and Zn3 in 4*f*). The Zn4 atoms fully occupy the 6*g* site. The other zinc atoms were found to occupy the split sites Zn5A/B and Zn6A/B in Wyckoff positions 12*j* and 12*k*, respectively. The coordination polyhedra of the atoms in the investigated phase (**Fig. 2**) are similar to those of the Th<sub>2</sub>Ni<sub>17</sub> type, but distorted. Selected interatomic distances are listed in **Table 3**. U–U contacts were not found. The U–Zn bonds are close to the sum of the atomic radii. The shortest U–Zn distances are observed for the U–Zn5A/B and U–Zn2 pairs.

**Table 2** Atom coordinates and isotropic displacement parameters for ht-U<sub>2</sub>Zn<sub>17</sub>.

Site	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> / <i>U</i> <sub>iso</sub> (Å <sup>2</sup> )	<i>G</i>
U1	2 <i>b</i>	0	0	¼	0.0073(7)	0.688(8)
Zn1	4 <i>e</i>	0	0	0.097(3)	0.027(8)	0.18(2)
U2	2 <i>c</i>	⅓	⅔	¼	0.0034(3)	0.986 <sup>a</sup>
Zn2	4 <i>f</i>	⅓	⅔	0.079(9)	0.020 <sup>a</sup>	0.014(4)
U3	2 <i>d</i>	⅓	⅔	¾	0.020 <sup>a</sup>	0.033(5)
Zn3	4 <i>f</i>	⅓	⅔	0.6033(4)	0.0077(11)	0.709(15)
Zn4	6 <i>g</i>	½	0	0	0.0096(6)	1.00 <sup>a</sup>
Zn5A	12 <i>j</i>	0.330(6)	0.014(4)	¼	0.023(4)	0.25(7)
Zn5B	12 <i>j</i>	0.3683(15)	0.0387(10)	¼	0.0091(16)	0.75(7)
Zn6A	12 <i>k</i>	0.1657(4)	2 <i>x</i>	0.008(2)	0.0094(15)	0.56(8)
Zn6B	12 <i>k</i>	0.1645(6)	2 <i>x</i>	0.036(3)	0.005(2)	0.44(8)

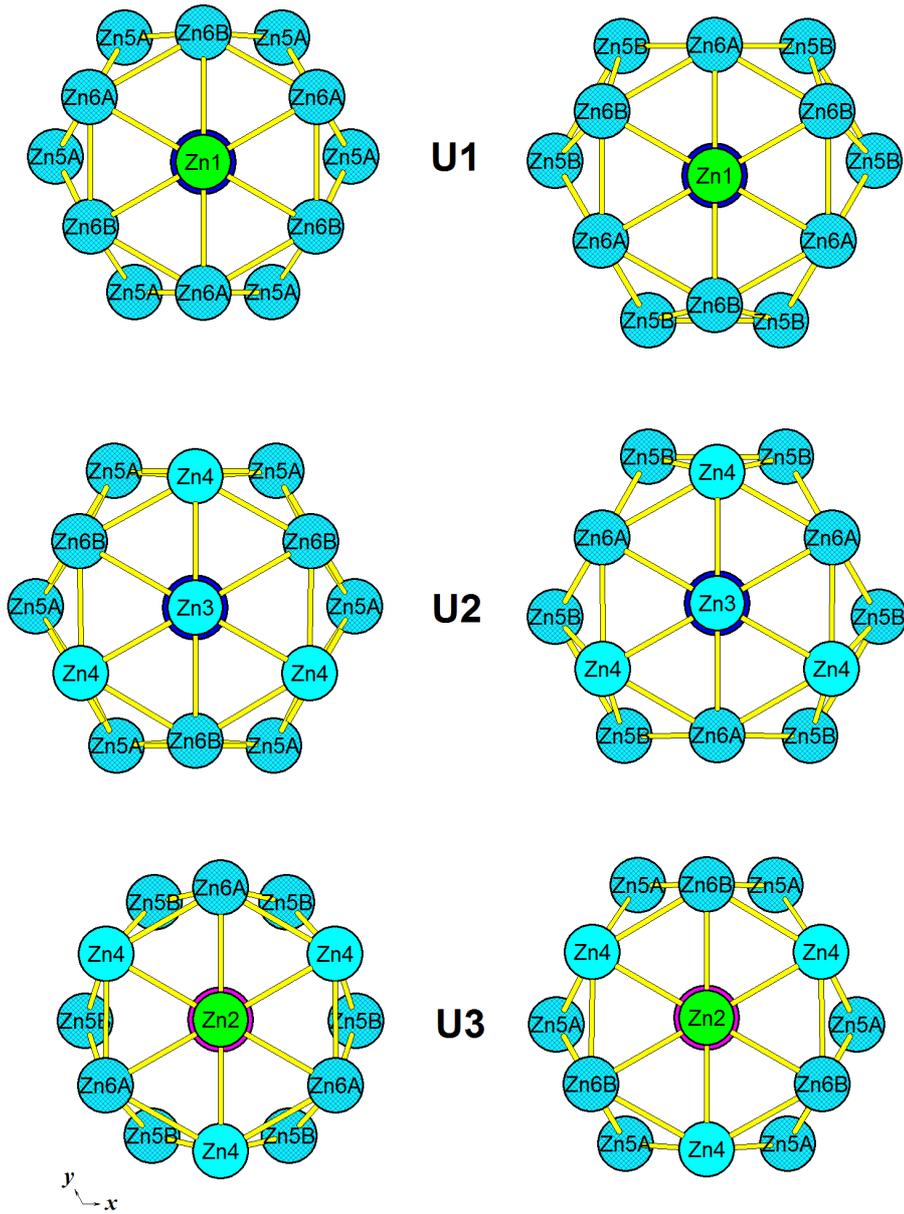
 Anisotropic displacement parameters for ht-U<sub>2</sub>Zn<sub>17</sub> (Å<sup>2</sup>).

Site	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>12</sub>
U1	0.0036(7)	0.0036(7)	0.0147(12)	0	0	0.0018(4)
U2	0.0010(4)	0.0010(4)	0.0082(6)	0	0	0.0005(2)
Zn3	0.0064(13)	0.0064(13)	0.0102(18)	0	0	0.0032(7)
Zn4	0.0036(8)	0.0096(12)	0.0176(13)	-0.0036(11)	-0.0018(6)	0.0048(6)

<sup>a</sup> Fixed in the last cycle of the refinement.

**Fig. 1** Unit cells of the Th<sub>2</sub>Ni<sub>17</sub> and ht-U<sub>2</sub>Zn<sub>17</sub> structures. The Th/Ni atoms, and the U/Zn atoms that occupy similar positions, are marked by blue and light cyan color, respectively. Dark cyan circles are Zn atoms from the partially disordered sites. The circles corresponding to additional locations of U and Zn atoms are filled by violet and green color, respectively. The atoms of Ni–Ni and Zn–Zn dumbbells are connected by bold yellow lines.

**Table 3** Interatomic distances and coordination numbers of the atoms in the ht-U<sub>2</sub>Zn<sub>17</sub> structure. Alternative connections are shown in bold style.

Atoms		<i>d</i> , Å	CN	Atoms		<i>d</i> , Å	CN
U1:	6Zn5A/	2.92(3)/	20	Zn4:	4Zn5B/	2.610(3)/	12
	<b>6Zn5B</b>	<b>3.166(7)</b>			<b>4Zn5A</b>	<b>2.725(14)</b>	
	2Zn1	3.06(2)			4Zn6A/	2.615(3)/	
	6Zn6B/	3.190(12)/			<b>4Zn6B</b>	<b>2.643(5)</b>	
	<b>6Zn6A</b>	<b>3.357(12)</b>			2Zn3/	2.761(1)/	
	6Zn6A/	3.448(12)/			<b>2U3</b>	<b>3.414(1)</b>	
	<b>6Zn6B</b>	<b>3.602(13)</b>		2U2/	3.414(1)/		
				<b>2Zn2</b>	<b>2.70(2)</b>		
U2:	2Zn3	3.115(4)	20	Zn5A:	2Zn6B/	2.45(2)/	12-14
	6Zn5A/	3.15(2)/			<b>2Zn6A</b>	<b>2.64(2)</b>	
	<b>6Zn5B</b>	<b>3.213(6)</b>			2Zn6A/	2.65(2)/	
	6Zn6B/	3.246(13)/			<b>2Zn6B</b>	<b>2.87(2)</b>	
	<b>6Zn6A</b>	<b>3.381(12)</b>			1Zn5B/	2.69(4)/	
	6Zn4	3.414(1)		<b>1Zn5A</b>	<b>2.73(6)</b>		
U3:	2Zn2	2.90(8)	20		2Zn4	2.725(14)	
	6Zn5B/	2.678(8)/		1U1/	2.92(3)/		
	<b>6Zn5A</b>	<b>2.97(3)</b>		<b>2Zn1</b>	<b>3.22(5)</b>		
	6Zn4	3.414(1)		1U3/	2.97(3)/		
	6Zn6A/	3.471(12)/		<b>2Zn3</b>	<b>3.24(3)</b>		
	<b>6Zn6B</b>	<b>3.652(13)</b>		1Zn5B/	2.97(6)/		
Zn1:	1Zn1	2.70(3)	8	Zn5B:	<b>1Zn5A</b>	<b>3.20(6)</b>	12-13
	3Zn6B/	2.628(11)/			1Zn5A/	3.11(5)/	
	<b>3Zn6A</b>	<b>2.708(11)</b>			<b>1Zn5B</b>	<b>3.39(3)</b>	
	3Zn6A/	2.752(12)/			1U2	3.15(2)	
	<b>3Zn6B</b>	<b>2.827(16)</b>					
	1U1	3.06(2)		2Zn4	2.610(3)		
Zn2:	3Zn6B/	2.668(13)/	8		1Zn5B/	2.627(14)/	
	<b>3Zn6A</b>	<b>2.70(2)</b>		<b>1Zn5A</b>	<b>2.69(4)</b>		
	3Zn4	2.70(2)		2Zn6B/	2.634(14)/		
	1U3	2.90(8)		<b>2Zn6A</b>	<b>2.816(15)</b>		
	1Zn2	3.02(11)		2Zn6A/	2.643(17)/		
Zn3:	1Zn3	2.587(5)	14		<b>2Zn6B</b>	<b>2.860(17)</b>	
	3Zn4	2.761(1)		1U3/	2.678(8)/		
	3Zn6A/	2.800(8)/		<b>2Zn3</b>	<b>2.974(8)</b>		
	<b>3Zn6B</b>	<b>2.913(10)</b>		1Zn5B/	2.728(16)/		
	6Zn5B/	2.974(8)/		<b>1Zn5A</b>	<b>2.97(3)</b>		
	<b>6Zn5A</b>	<b>3.24(3)</b>		1U1	3.166(7)		
	1U2	3.115(4)		1U2	3.213(6)		
Zn6A:	2Zn6A/	2.596(5)/	11-12	Zn6B:	1Zn5A/	3.39(3)/	11-12
	<b>2Zn6B</b>	<b>2.611(7)</b>			<b>1Zn5B</b>	<b>3.675(12)</b>	
	2Zn4	2.615(3)					
	2Zn5A/	2.64(2)/			2Zn5A/	2.45(2)/	
	<b>2Zn5B</b>	<b>2.816(15)</b>			<b>2Zn5B</b>	<b>2.634(14)</b>	
	2Zn5B/	2.643(14)/			2Zn6A/	2.611(7)/	
	<b>2Zn5A</b>	<b>2.65(2)</b>			<b>2Zn6B</b>	<b>2.650(9)</b>	
	1Zn2/	2.70(2)/			1Zn1/	2.628(11)/	
	<b>1Zn3</b>	<b>2.800(8)</b>			<b>1Zn1</b>	<b>2.827(16)</b>	
	1U2	<b>3.381(12)</b>			2Zn4	2.643(5)	
	1Zn1/	2.708(11)/			1Zn2/	2.668(13)/	
	<b>1Zn1</b>	<b>2.752(12)</b>			<b>1Zn3</b>	<b>2.913(11)</b>	
	1U1/	3.448(12)/			1U2	<b>3.246(13)</b>	
<b>1U1</b>	<b>3.357(12)</b>	2Zn5B/	2.860(17)/				
		<b>2Zn5A</b>	<b>2.87(2)</b>				
		1U1/	3.602(13)/				
		<b>1U1</b>	<b>3.190(12)</b>				



**Fig. 2** Coordination polyhedra of the atoms with selected connections in the structure of ht- $U_2Zn_{17}$ .

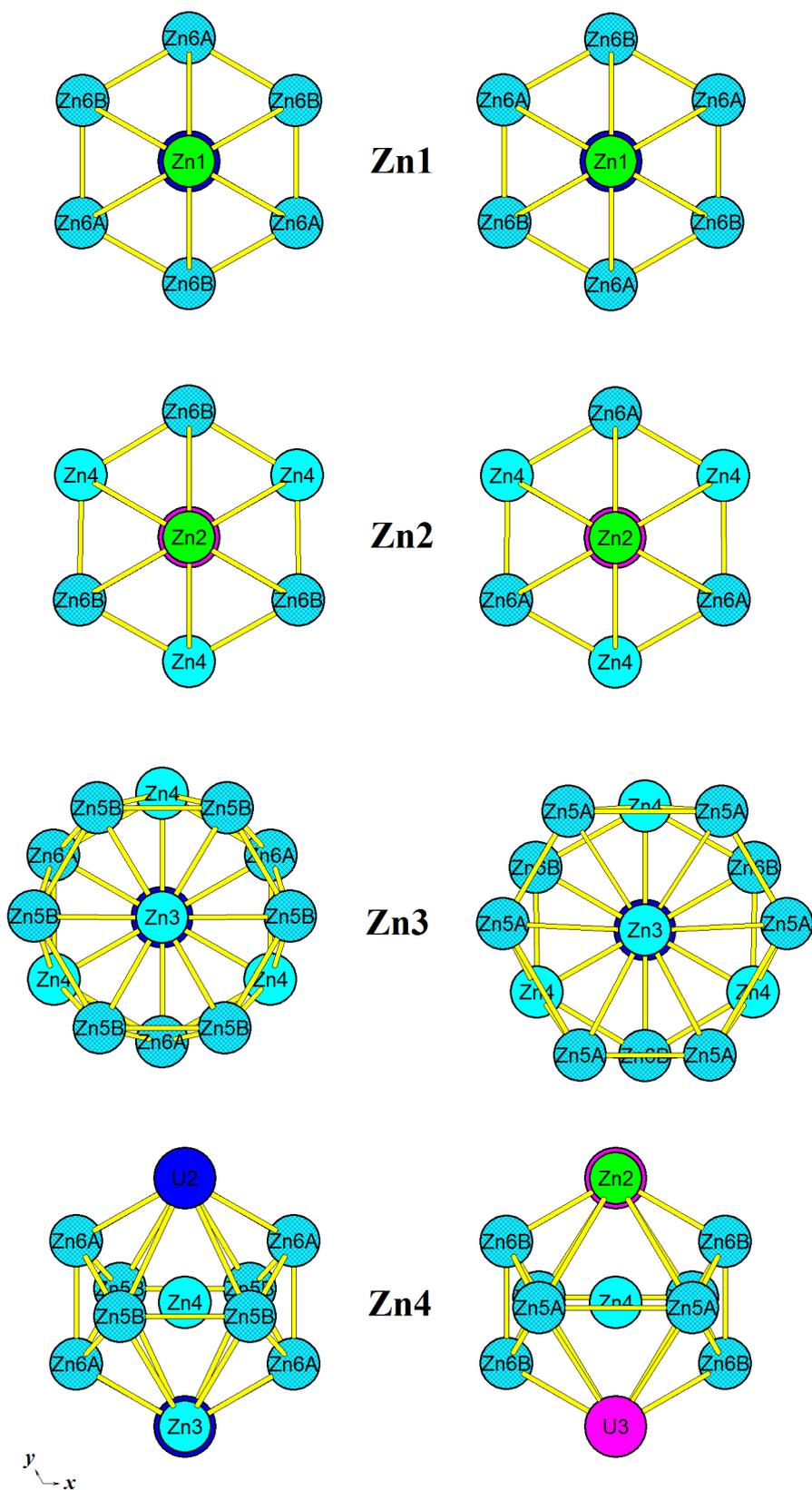


Fig. 2 (continued)

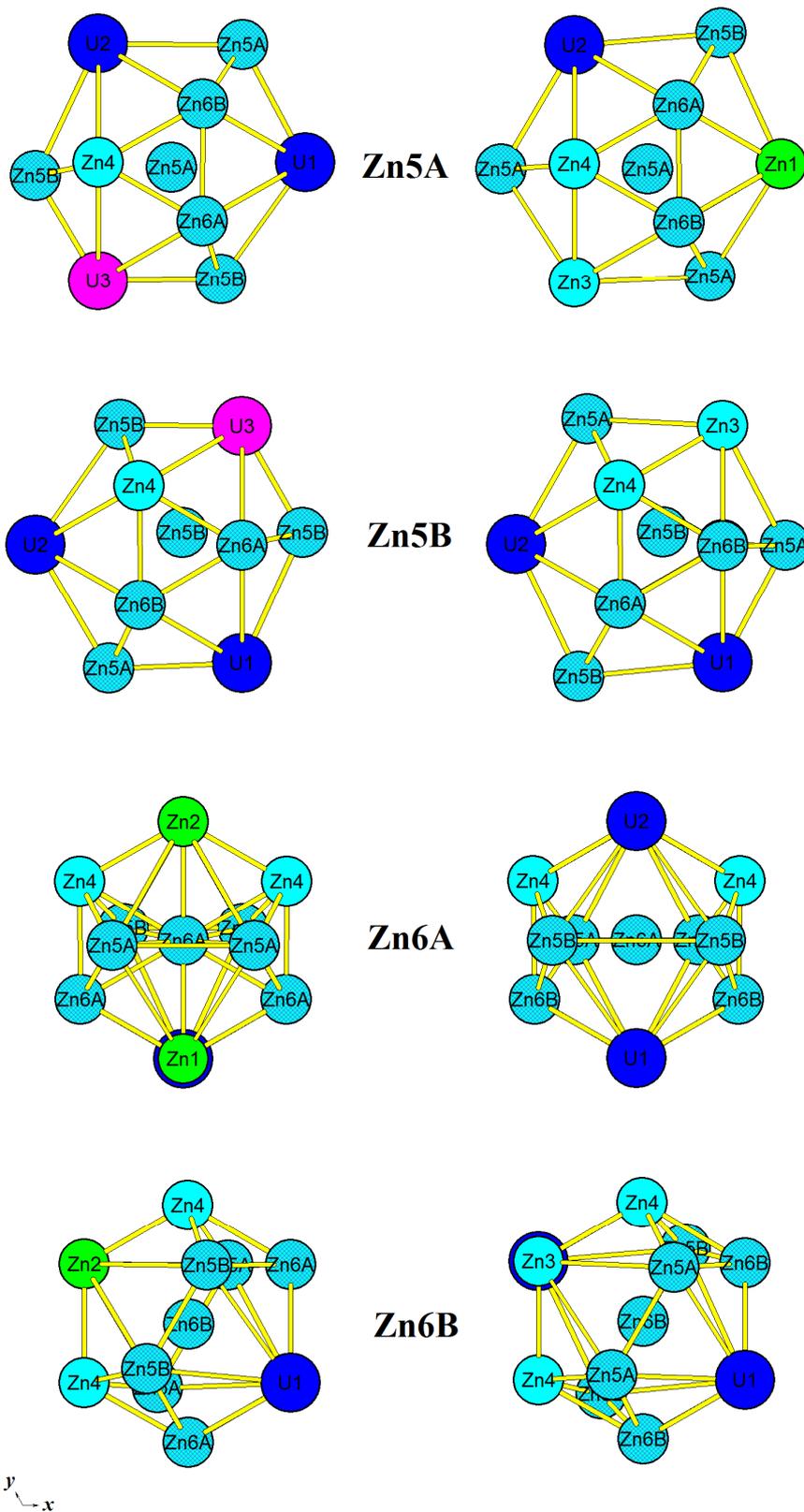


Fig. 2 (continued)

Considerably short distances can also be seen between the following Zn atoms: Zn1–Zn1, Zn1–Zn6A/B, Zn2–Zn4, Zn2–Zn6A/B, Zn3–Zn3, Zn3–Zn4, Zn4–Zn5A/B, Zn4–Zn6A/B, Zn5A/B–Zn5A/B, Zn5A/B–Zn6A/B and Zn6A/B–Zn6A/B. These short distances point to strong interactions between the Zn atoms.

It should be stressed that the structural studies presented here were performed for a Zn-rich composition of the ht-U<sub>2</sub>Zn<sub>17</sub> phase. Most probably (and similarly to the UZn<sub>12</sub> compound), the crystal structure of other compositions from the homogeneity range should be slightly different and should continuously change with decreasing zinc concentration. Besides, as the studied crystal was obtained from a fast quenched alloy, it may be metastable, and we cannot turn down the possibility that the annealing procedure at high temperature (> 800°C) could result in a slightly different atomic ordering.

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