



# SmZn<sub>11</sub>-type derivative compound in the Yb–Zn–Al system: Crystal structure and magnetic properties

O. Stelmakhovych<sup>a,b</sup>, B. Stelmakhovych<sup>a</sup>, K. Uhlířová<sup>b</sup>, S. Mašková<sup>b</sup>, L. Havela<sup>b,\*</sup>, Ya. Kalychak<sup>a</sup>

<sup>a</sup> Department of Analytical Chemistry, Ivan Franko National University of Lviv, Kyryla & Mefodija Str. 6, 79005 Lviv, Ukraine

<sup>b</sup> Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, 12116 Prague 2, Czech Republic

## ARTICLE INFO

### Article history:

Received 26 February 2011

Received in revised form

6 May 2011

Accepted 8 May 2011

Available online 17 May 2011

### Keywords:

Intermetallics

Crystal growth

Crystal structure

Magnetization

Differential thermal analysis

Chemical analysis

## ABSTRACT

Crystal structure and magnetic properties are reported for Yb<sub>3.50</sub>Zn<sub>32.1</sub>Al<sub>1.4</sub> prepared in single-crystalline form. It adopts the SmZn<sub>11</sub>-type of structure (SG *P6/mmm*) with lattice parameters  $a=0.90458(1)$ ,  $c=0.88547(1)$  nm. The phase composition was analyzed by XRD, chemical and electron microprobe analysis. The ytterbium atoms in this compound are in the non-magnetic  $4f^{14}$  state.

© 2011 Elsevier Inc. All rights reserved.

## 1. Introduction

Crystal structures of newly discovered intermetallic compounds in the very rich Yb–Zn–Al system have been recently investigated extensively. The data on structures of several intermetallics were reported, namely: Yb<sub>25.39</sub>Zn<sub>138.2</sub>Al<sub>7.7</sub> (YCd<sub>6</sub>-type of structure, SG *Im-3*) [1], Yb<sub>3.36</sub>Zn<sub>30.94</sub>Al<sub>4.34</sub> (SmZn<sub>11</sub>-type of structure, SG *P6/mmm*) [2], Yb<sub>6.4</sub>Zn<sub>46.8</sub>Al<sub>3.4</sub> (Yb<sub>6.4</sub>Zn<sub>46.8</sub>Al<sub>3.4</sub>-type of structure, SG *P6/mmm*) [2], Yb<sub>12.4</sub>Zn<sub>96.8</sub>Al<sub>4.4</sub> (U<sub>2</sub>Zn<sub>17</sub>-type of structure, SG *P6<sub>3</sub>/mmc*) [2], Yb<sub>3</sub>Zn<sub>17.7</sub>Al<sub>4.3</sub> (Ce<sub>3</sub>Zn<sub>22</sub>-type of structure, SG *I4<sub>1</sub>/amd*) [2], Yb<sub>3</sub>Zn<sub>6.16-4</sub>Al<sub>4.84-7</sub> (La<sub>3</sub>Al<sub>11</sub>-type of structure, SG *Immm*) [3], and Yb<sub>8</sub>Zn<sub>48.5-41.4</sub>Al<sub>17.5-24.6</sub> (Yb<sub>8</sub>Cu<sub>17</sub>Al<sub>49</sub>-type of structure, SG *I4/mmm*) [3], YbZn<sub>0.996</sub>Al<sub>1.004</sub> (MgNi<sub>2</sub>-type of structure, SG *P6<sub>3</sub>/mmc*) [4], YbZn<sub>0.88</sub>Al<sub>1.12</sub> (MgCu<sub>2</sub>-*Fd-3m*) [4], YbZn<sub>2.50</sub>Al<sub>0.50</sub> (CeNi<sub>3</sub>-type of structure, SG *P6<sub>3</sub>/mmc*) [4], YbZn<sub>1.92</sub>Al<sub>1.08</sub> (PuNi<sub>3</sub>- or NbBe<sub>3</sub>-type of structure, *R-3m*) [4]. We continued mapping the Yb–Zn–Al ternary phase diagram, which still indicated existence of previously unknown compounds YbZn<sub>8.5</sub>Al<sub>2.5</sub> (BaHg<sub>11</sub>-type of structure, SG *Pm-3m*) [5], Yb<sub>4</sub>Zn<sub>20.3</sub>Al<sub>12.7</sub> (Yb<sub>8</sub>Cu<sub>17</sub>Al<sub>49</sub>-type of structure, SG *I4/mmm*) [6] and YbZn<sub>1.65</sub>Al<sub>2.35</sub> (BaAl<sub>4</sub>-type of structure, SG *I4/mmm*) [7].

Magnetic properties of the compounds in the Yb–Zn–Al system are practically unknown. The first results for the compound Yb<sub>25.39</sub>Zn<sub>138.2</sub>Al<sub>7.7</sub> (YCd<sub>6</sub>-type of structure) were reported by

Fornasini et al. [1]. Magnetization, electrical resistivity and specific heat measurements revealed that ytterbium atoms in this compound are in the non-magnetic  $4f^{14}$  state.

Our recent investigations on YbZn<sub>8.5</sub>Al<sub>2.5</sub> with the BaHg<sub>11</sub>-type of structure [5] revealed mixed valence state of the Yb atoms. Here we report on the structure and magnetic properties of single-crystalline Yb<sub>3.50</sub>Zn<sub>32.1</sub>Al<sub>1.4</sub>, which adopts the SmZn<sub>11</sub>-type of structure.

## 2. Experimental

### 2.1. Synthesis

Single crystals of the compound Yb<sub>3.50</sub>Zn<sub>32.1</sub>Al<sub>1.4</sub> were synthesized from a ternary Zn-rich flux. Appropriate amounts of the pure components were placed into alumina crucibles with quartz-wool stoppers and enclosed in sealed evacuated silica ampoules. The samples were heated up to 1030 K at a rate of 3 K/min, held for 1 h, and cooled down to 770 K at a rate of 0.05 K/min. Then the tube was removed fast from the furnace and the excess Zn was centrifuged through the quartz-wool stopper from the crystals.

### 2.2. Electron microprobe analysis

Microprobe analysis was carried out using a Tescan Mira I LMH microscope, with Bruker AXS and X flash detectors, and ESPRIT 18 software.

\* Corresponding author. Fax: +420 22191351.

E-mail address: [havela@mag.mff.cuni.cz](mailto:havela@mag.mff.cuni.cz) (L. Havela).

### 2.3. Chemical analysis

The single-crystal sample was dissolved in a 10% aqueous solution of hydrochloric acid. After evaporation of the solution, the residue was dissolved in distilled water and ammonia solution was added. The ytterbium and aluminum hydroxides were precipitated and  $Zn^{2+}$  ions remained in solution as  $[Zn(NH_3)_4]^{2+}$ . The residue was separated by filtration. The amount of Zn in the solution was determined by complexometric titration with EDTA as a chelating agent and eriochrome black as indicator. The hydroxides residue was washed with 3% ammonia solution. Aluminum hydroxide was solved on the filter by treatment with a hot alkali solution. The amount of aluminum was estimated by complexometric back titration using standard zinc solution. The filter with the ytterbium hydroxide residue was washed until neutral reaction and dried in the desiccators. Then it was ashed in a porcelain crucible and calcined at 920 K until the mass was stable. The amount of the ytterbium was determined by gravimetric analysis in the form of  $Yb_2O_3$ .

### 2.4. Differential thermal analysis

DTA analysis was carried out on STA 409C NETZSCH apparatus (SiC-furnace, Pt10%Rh–Pt thermocouple) in alumina crucible under dynamic argon atmosphere in the temperature range 303–1030 K. The heating and cooling rates were 10 K/min.

### 2.5. Crystal structure determination

Single crystal intensities for the crystal structure determination were collected on a CAD-4 single crystal diffractometer with  $AgK\alpha$ -radiation ( $\lambda=0.056087$  nm) and a CCD detector in  $\theta-2\theta$  mode. All calculations were performed using CSD software [8].

### 2.6. Magnetization measurements

Magnetization measurements were performed on single crystal sample in the temperature range 1.8–300 K and magnetic fields up to 9 T, applied along the  $c$ -axis and perpendicular to  $c$ , by means of Quantum Design PPMS equipment.

## 3. Results and discussion

### 3.1. Synthesis

The sample with the starting composition  $Yb_5Zn_{81}Al_{14}$  was heated to 1030 K in a Zn flux and then cooled to 770 K. After separation of the Zn matrix and cooling to the room temperature, the single crystals in the form of hexagonal prisms up to 3 mm in length were found in the crucible. The composition of the sample from microprobe analysis is  $Yb_9Zn_{85}Al_6$  (in at%). The chemical analysis of the crystals gave the composition  $Yb_{9.4}Zn_{87.8}Al_{2.8}$  ( $\omega_{Yb}=22.0(3)\%$ ,  $\omega_{Zn}=77.0(2)\%$ ,  $\omega_{Al}=1.0(4)\%$ ).

### 3.2. Crystal structure determination

Preliminary single crystal investigations and the refinement of the lattice parameters in the hexagonal unit cell gave us a hint that this compound belongs to the  $SmZn_{11}$ -type of structure. This suggestion was confirmed by the refinement of atomic parameters. Basic crystallographic data and conditions of the investigation are shown in Table 1.

The structure of a new compound with the  $SmZn_{11}$ -type of structure was reported recently by Fornasini et al. [2]. These data were used as a starting model in our refinement. The discrepancy between the composition of the obtained crystals ( $Yb_{3.50(1)}$

**Table 1**

Crystallographic data for the  $Yb_{3.50}Zn_{32.1}Al_{1.4}$ .

Composition	$Yb_{3.50}Zn_{32.1}Al_{1.4}$
Space group	$P6/mmm$ (N 191)
Lattice parameters (nm)	$a=0.90458(1)$ , $c=0.88547(1)$
Cell volume (nm <sup>3</sup> ); Z	0.62748(2); 1
Number of atomic sites	9
Number of free parameters	32
Density (calc.) (g/cm <sup>3</sup> )	7.3167
Absorption coefficient (cm <sup>-1</sup> )	234.5
Mode of refinement	$F(h k l)$
Radiation (nm)	$AgK\alpha$ , 0.0560871
$2\theta_{max}$ and $\sin \theta_{max}/\lambda$	56.30 0.841
Range in $h k l$	0–17, 0–17, 0–34
Number of measured reflections	1859
Numbers of unique reflections	599
Restrictions	$F(h k l) > 4\sigma(F)$
Goodness of fit	1.020
Scale factor	0.317(3)
$R_{sig}$ , $R_{eq}$ , $R_F$ , $R_w$	0.050, 0.0430, 0.0467, 0.0507

**Table 2**

Atomic coordinates and thermal displacement parameters ( $B_{eq}$ ) in the  $Yb_{3.50}Zn_{32.1}Al_{1.4}$  structure.

Atoms	WP	Coordinates			$B_{eq}(10^{-2} \text{ nm}^2)$
		x	y	z	
Yb1	1a	0	0	0	0.54(3)
Yb2	2d	2/3	1/3	1/2	0.56(2)
Yb3 <sup>a</sup>	2c	2/3	1/3	0	0.85(8)
X1 <sup>a</sup>	2e	0	0	0.3526(5)	0.68(7)
X2 <sup>a</sup>	4h	2/3	1/3	0.1460(8)	0.84(11)
X3 <sup>a</sup>	6i	1/2	0	0.2740(3)	1.00(5)
X4 <sup>a</sup>	6k	0.2985(3)	0	1/2	0.81(4)
X5 <sup>a</sup>	6j	0.3525(3)	0	0	2.33(11)
X6 <sup>a</sup>	12o	0.1678(1)	2x	0.2411(2)	0.84(3)

<sup>a</sup>  $Yb3=0.498(10)Yb$ ;  $X1=1.24(4)Zn+0.76(4)Al$ ;  $X2=1.44(4)Zn$ ;  $X3=6Zn$ ;  $X4=6Zn$ ;  $X5=5.40(12)Zn+0.60(12)Al$ ;  $X6=12Zn$ .

$Zn_{32.08(20)}Al_{1.36(16)}$ ) and data given in Ref. [2] ( $Yb_{3.36}Zn_{30.94}Al_{4.34}$ ) can indicate the existence of a homogeneity range for this compound. Atomic coordinates and equivalent displacement parameters are given in Table 2. Besides the Yb positions 1(a) and 2(d) there are two positions, 2(c) and 4(h), with partial occupancy by ytterbium and zinc atoms, respectively. The smaller atoms of Zn and Al are statistically distributed in the remaining crystallographic positions. The composition of the sample obtained from X-ray analysis ( $Yb_{9.47}Zn_{86.90}Al_{3.63}$ , in at%) is in good agreement with the composition from the chemical analysis.

Interatomic distances are in good agreement with the sum of the atomic radii of the elements (Table 3). The distances between alternative Yb3 and X2 atoms (0.1294(7) nm) in crystallographic positions 2(c) (1/3 2/3 1/2) and 4(h) (1/3 2/3 z,  $z=0.1460(8)$ ) are not realized in the structure of  $Yb_{3.50(1)}Zn_{32.08(20)}Al_{1.36(16)}$ , as general occupancy of these sites Yb3 (24.8(5)%) and X2 (36.6(9)%) is less than 100%. Slight shortening of the distances (9.5%) between Yb3 and X5 atoms in the defective positions is observed. That can indicate the appearance of a partially covalent interaction between these atoms. The high value of displacement parameter  $B_{22}$  for the X5 atoms also points to this fact. The anisotropic displacement parameters are listed in Table 4.

### 3.3. Differential thermal analysis

We investigated splices of the  $Yb_{3.50}Zn_{32.1}Al_{1.4}$  single crystals also using differential thermal analysis. The DTA pattern of the sample is shown in Fig. 1. One can observe significantly reproducible thermal

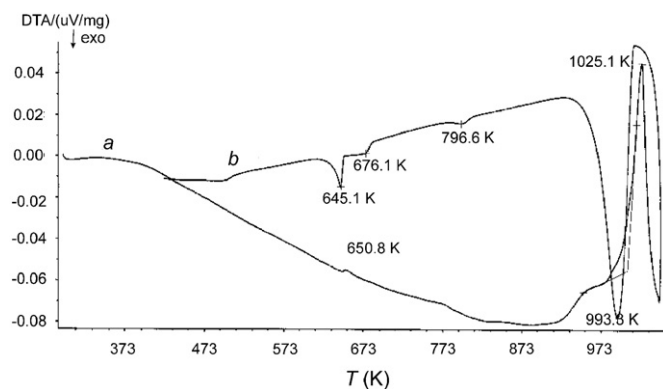
**Table 3**  
Interatomic distances ( $\delta$ ) in the  $\text{Yb}_{3.50}\text{Zn}_{32.1}\text{Al}_{1.4}$  structure.

Atom	$\delta$ (nm)	Atom	$\delta$ (nm)
Yb1–		X3–	
–2X1	0.3123(5)	–2X2	0.2847(3)
–6X5	0.3190(2)	–2Yb2	0.3290(1)
–12X6	0.3388(1)	–2Yb3	0.3565(2)
Yb2–		X4–	
–2X2	0.3134(7)	–4X6	0.2676(2)
–6X4	0.3184(1)	–2X4	0.2700(2)
–6X3	0.3290(1)	–2X3	0.2706(2)
–6X6	0.3460(1)	–2X1	0.2999(2)
Yb3–		–2Yb2	0.3184(1)
–2X2 <sup>a</sup>	0.1294(7)	X5–	
–6X5	0.2932(2)	–4X6	0.2669(2)
–6X6	0.3359(1)	–1X5	0.2667(2)
–6X3	0.3565(2)	–2Yb3	0.2932(2)
X1–		–1Yb1	0.3190(2)
–1X1	0.2609(6)	–2X5	0.3190(2)
–6X6	0.2810(2)	–4X2	0.3205(3)
–6X4	0.2999(2)	X6–	
–1Yb1	0.3123(5)	–2X3	0.2618(1)
X2–		–2X6	0.2630(1)
–Yb3 <sup>a</sup>	0.1294(7)	–2X5	0.2669(2)
–1X2	0.2587(10)	–2X4	0.2676(2)
–3X6	0.2726(2)	–1X2	0.2726(2)
–3X3	0.2847(3)	–2X1	0.2810(2)
–1Yb2	0.3134(7)	–1Yb3	0.3359(1)
–5X5	0.3205(3)	–1Yb1	0.3388(1)
X3–		–1Yb2	0.3460(1)
–3X6	0.2618(1)		
–2X4	0.2706(2)		
–1X5	0.2769(2)		

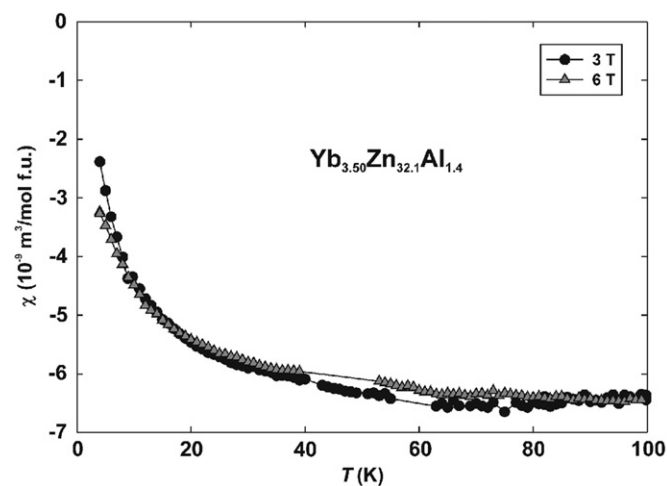
<sup>a</sup> Yb3– and X2–atoms are in alternative positions.

**Table 4**  
Anisotropic displacement parameters of the atoms in the  $\text{Yb}_{3.50}\text{Zn}_{32.1}\text{Al}_{1.4}$  structure ( $10^{-2}$  nm<sup>2</sup>).

Atoms	B <sub>11</sub>	B <sub>22</sub>	B <sub>33</sub>	B <sub>12</sub>	B <sub>13</sub>	B <sub>23</sub>
Yb1	0.59(3)	0.59(3)	0.30(4)	0.29(1)	0	0
Yb2	0.44(2)	0.44(2)	0.58(3)	0.22(1)	0	0
Yb3	0.70(9)	0.70(9)	1.0(2)	0.35(4)	0	0
X1	0.67(8)	0.67(8)	0.46(12)	0.33(4)	0	0
X2	0.83(13)	0.83(13)	0.6(2)	0.42(6)	0	0
X3	0.48(4)	1.06(6)	1.34(7)	0.53(3)	0	0
X4	0.91(5)	0.67(6)	0.54(5)	0.33(3)	0	0
X5	1.79(7)	5.5(2)	0.56(7)	2.74(10)	0	0
X6	0.40(3)	1.04(4)	1.02(4)	0.52(2)	0.04(2)	0.08(4)

**Fig. 1.** DTA curve for  $\text{Yb}_{3.50}\text{Zn}_{32.1}\text{Al}_{1.4}$  on heating (a) and cooling (b) of the sample.

effects at 645–651 K and 993–1025 K on the heating (a) and cooling (b) curves. The latter one is obviously connected with melting of the compound. We annealed the sample at 570 K for 240 h to check the

**Fig. 2.** Temperature dependence of magnetic susceptibility for  $\text{Yb}_{3.50}\text{Zn}_{32.1}\text{Al}_{1.4}$  ( $B||c$ ).

nature of the effect in the temperature range 645–651 K. The annealed sample was analyzed by X-ray diffraction. No structure changes were observed between the annealed and original samples. The thermal effect at 645–651 K is in good correlation with eutectic temperature of the binary alloy in the Zn–Al system with the amount of zinc equal to 67 at% [9]. The small peak at 676 K comes obviously from pure Zn, with melting point 673 K. Admixtures of other phase were not observed on the X-ray powder pattern because of the lower sensitivity of the X-ray analysis in comparison with DTA. The results of the investigation indicate the congruent melting of  $\text{Yb}_{3.50}\text{Zn}_{32.1}\text{Al}_{1.4}$ .

### 3.4. Magnetic properties

The studied material is diamagnetic. The magnetization measurements for the  $\text{Yb}_{3.50}\text{Zn}_{32.1}\text{Al}_{1.4}$  crystal in the magnetic field perpendicular to the *c*-axis showed low negative values of magnetic susceptibility of the order of  $10^{-9}$  m<sup>3</sup>/mol f.u. (Fig. 2). Also results in magnetic field parallel to the *c*-axis exhibited similar values, indicating absence of magnetic anisotropy. The weak temperature dependence can be attributed to Curie behavior of a small concentration of magnetic rare earths contaminating Yb. The susceptibilities in  $\mu_0H=3$  and 6 T are almost identical. Only in the low temperature limit the data in 6 T go systematically below susceptibility in 3 T. The reason can be seen in tendency to saturation of magnetization of the spurious magnetic ions in higher field. Ytterbium atoms are undoubtedly in the  $4f^{14}$  configuration with the closed *f* shell suppressing any sign of paramagnetism. In regular Yb alloys and compounds, even in those with the  $4f^{14}$  state, Pauli paramagnetism mainly due to the *5d* states at the Fermi level can dominate over all diamagnetic contributions. In the present compound it is the high concentration of Zn and Al can be seen as the reason why the diamagnetism wins over the paramagnetic contributions.

## 4. Conclusions

While mapping the phase equilibria diagram of the Yb–Zn–Al system, the existence of the  $\text{SmZn}_{11}$ -type of structure compound was confirmed. The composition data from EDX, chemical and X-ray analysis show good correlation.  $\text{Yb}_{3.50}\text{Zn}_{32.1}\text{Al}_{1.4}$  melts congruently at 1025 K. Magnetization measurements revealed divalent state of Yb atoms in this structure.

## Acknowledgment

This work was part of the research plans MSM 0021620834 financed by the Ministry of Education of the Czech Republic and 0109U002093 from Ministry of Education and Science of Ukraine. O. Stelmakhovych acknowledges with gratitude the financial support of International Visegrad Fund.

## Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jssc.2011.05.013](https://doi.org/10.1016/j.jssc.2011.05.013).

## References

[1] M.L. Fornasini, P. Manfrinetti, D. Mazzone, S.K. Dhar, Z. Naturforsch. B 63 (2008) 237–243.

- [2] M.L. Fornasini, P. Manfrinetti, D. Mazzone, J. Solid State Chem. 176 (2006) 2012–2019.
- [3] M.L. Fornasini, P. Manfrinetti, D. Mazzone, Intermetallics 15 (7) (2006) 856–861.
- [4] D. Mazzone, P. Manfrinetti, M.L. Fornasini, J. Solid State Chem. 182 (2009) 2344–2349.
- [5] O. Stelmakhovych, B. Stelmakhovych, Ya. Kalychak, L. Havela, Intermetallics 18 (2010) 569–573.
- [6] O. Stel'makhovych, Yu. Kuz'ma, Z. Naturforsch. B 61 (2006) 779–784.
- [7] B. Stel'makhovych, O. Stel'makhovych, Yu. Kuz'ma, J. Alloys Compd. 397 (2005) 115–119.
- [8] L.G. Aksel'rud, Yu.N. Grin, P.Yu. Zavalij, CSD97-Universal program package for single crystal and powder data treatment. Version No. 7, 1997.
- [9] H. Okamoto, J. Phase Equilib. 16 (3) (1995) 281–282.