



The new binary intermetallic $\text{YbGe}_{2.83}$

C. Peter Sebastian, Mercuri G. Kanatzidis*

Department of Chemistry, Northwestern University, 2145 N. Sheridan Road, Evanston, IL 60208-3113, USA

ARTICLE INFO

Article history:

Received 3 June 2010

Received in revised form

28 June 2010

Accepted 28 June 2010

Available online 23 July 2010

Keywords:

Yb–Ge system

Mixed valence

Superstructure

Zintl phase

Intermetallics

ABSTRACT

The new compound $\text{YbGe}_{2.83}$ was obtained from the reaction of Yb and Ge in liquid indium. The crystal structure of $\text{YbGe}_{2.83}$ adopts the trigonal, $P\bar{3}m1$ space group with $a=b=8.3657(12)$ Å and $c=7.0469(14)$ Å. The structure of $\text{YbGe}_{2.83}$ is a variant of the CaAl_2Si_2 structure type with ordered vacancies. Germanium atoms form double layers of puckered hexagons creating slabs that sandwich the Yb atoms. $\text{YbGe}_{2.83}$ can be classified as a Zintl compound with the formula $\text{Yb}^{(2+x)+}(\text{Ge}_{2.83})^{(2+x)-}$. The deficiencies at the Ge sites cause a mixed/intermediate valent state of ytterbium ($\text{Yb}^{2.35+}$). Valence bond sum calculations suggest an average valence of Yb ions in $\text{YbGe}_{2.83}$ of 2.51 consistent with an intermediate valence compound.

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1. Introduction

The first compound discovered in the Yb–Ge system was Yb_2Ge_3 , an AlB_2 type reported in 1964 by Gladyshevskii [1]. In the following year Smith et al. [2] reported the crystal structure of Yb_3Ge_5 , a Th_3Pd_5 type structure. In 1983 Eremenko et al. [3] discovered $\text{Yb}_{11}\text{Ge}_{10}$, a $\text{Ho}_{11}\text{Ge}_{10}$ type structure and a carbon stabilized Yb_3Ge_5 , Mn_5Si_3 type structure and they proposed the phase diagram of Yb–Ge system for the first time. In 1990, all those previous results were compiled by Massalski et al. [4] in the book *Binary Alloy Phase Diagrams*. In 2003, Pani and Palenzona [5] synthesized and elucidated the structure of Yb_2Ge (PbCl_2 type), Yb_5Ge_3 (Mn_5Si_3 type), Yb_5Ge_4 (Sm_5Ge_4 type) and Yb_3Ge_8 (its own structure type) to complete the Yb–Ge phase diagram.

There are few REGe_3 ($\text{RE}=\text{Y}, \text{Gd–Er}$) binary compounds crystallized in orthorhombic Cmcm space group with the DyGe_3 structure type [6–11]. Except for DyGe_3 , a deficiency in the Ge is not uncommon in these systems, as evidenced by the compositions $\text{YGe}_{2.69}$ [6], $\text{GdGe}_{2.57}$ [7], $\text{TbGe}_{2.7}$ [8], $\text{HoGe}_{2.7}$ [10] and $\text{ErGe}_{2.83}$ [11]. From the perspective of Yb, 1:3 compounds are known with terelides (Al, Ga, In, Tl) [12,13] and tetrelides (Sn and Pb) [14,15]. Except for YbGa_3 , all others crystallize in the cubic Cu_3Au structure type ($\text{Pm}\bar{3}n$ space group) and feature fully occupied Ge sites. YbGa_3 is hexagonal and crystallizes in its own structure type but with a deficiency in the Ga position ($\text{YbGa}_{2.64}$) [16]. Surprisingly, the binary YbSi_3 and YbGe_3 are missing compounds in this category.

During our studies on $\text{Yb}_x\text{T}_y\text{Ge}_z$ ($T=\text{transition metal}$) compounds in indium metal flux, we have observed many rod shaped crystals of side products, such as Yb_5Ge_3 and $\text{Yb}_3\text{Ge}_{5-x}$. In addition, we observed triangular shaped single crystals of a new binary YbGe_3 which it was subsequently determined to have the composition of $\text{YbGe}_{2.83}$. Here we report the synthesis and crystal structure of $\text{YbGe}_{2.83}$.

2. Experimental section

2.1. Synthesis

The $\text{YbGe}_{2.83}$ was obtained as a side product from the reactions by combining 3 mmol of the Yb metal, 2 mmol of transition metal (Ag or Pd), 6 mmol of Ge and 45 mmol of In in an alumina crucible under inert nitrogen atmosphere inside a glove-box. The crucible was placed in a 13 mm fused silica tube, which was flame sealed under vacuum of 10^{-4} Torr, to prevent oxidation during heating. The reactants were then heated to 1000 °C over 10 h, maintained at that temperature for 5 h to allow for proper homogenization, followed by cooling to 850 °C in 2 h and held there for 48 h. Finally, the system was allowed to cool to 50 °C in 48 h. The reaction product was isolated from the excess indium flux by heating at 350 °C and subsequent centrifugation through a coarse frit. Any remaining flux was removed by immersion and sonication in glacial acetic acid for 48 h. The final crystalline product was rinsed with water and acetone. The ternary compounds obtained from the Pd and Ag based reactions were YbPd_2Ge_2 [17] and Yb_4AgGe_8 [18], respectively. The binary side products obtained from the reaction were well formed crystals of Yb_5Ge_3 and Yb_3Ge_5 compounds. In addition, we observed a few

* Corresponding author. Fax: +1 847 491 5937.

E-mail address: m-kanatzidis@northwestern.edu (M.G. Kanatzidis).

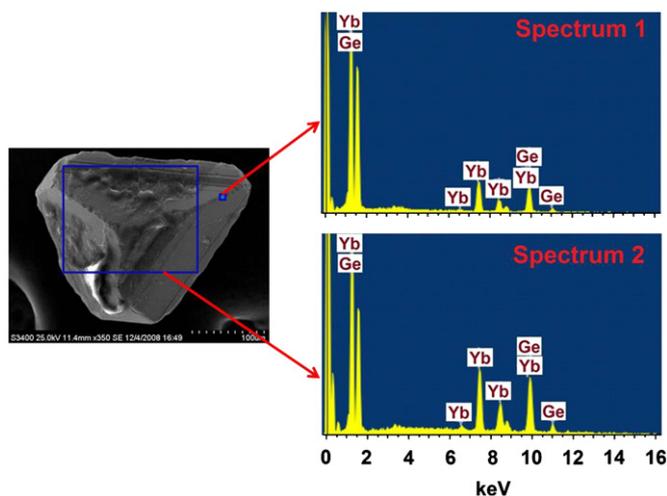


Fig. 1. Image of the typical single crystal of $\text{YbGe}_{2.83}$ and EDS data from the selected spot (spectrum 1) and the area indicated by the blue square (spectrum 2) of the crystal. The analytical data indicate absence of other elements. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

small triangular shaped crystals which were identified as “ YbGe_3 ” from the energy dispersive X-ray spectroscopy (EDS) measurements. A scanning electron microscopy (SEM) image of a typical single crystal of YbGe_3 is shown in Fig. 1.

The particular synthesis conditions under which $\text{YbGe}_{2.83}$ was discovered appear to be essential for its stabilization. More direct attempts made to synthesize the compound in bulk quantity for physical property studies by varying the starting composition and using various techniques (including Ge flux) such as arc-melting and high frequency induction heating were unsuccessful. The main product observed from these experiments was the more thermodynamically stable Yb_3Ge_5 .

2.2. Elemental analysis

Quantitative microprobe analyses of the compounds were performed with a Hitachi S-3400 scanning electron microscope (SEM) equipped with a PGT energy dispersive X-ray analyzer. Data were acquired with an accelerating voltage of 20 kV and a 60 s accumulation time. The EDS analysis taken on visibly clean surfaces of the single crystal used for the data collection gave an atomic composition that is in good agreement with the results derived from the single crystal X-ray diffraction refinement. The EDS detector cannot detect elements lighter than Be.

2.3. X-ray crystallography

The X-ray intensity data were collected at room temperature using a STOE IPDS 2T diffractometer with graphite-monochromatized $\text{MoK}\alpha$ ($\lambda=0.71073$ Å) radiation. The X-AREA (X-RED and X-SHAPE within) package suite was used for the data extraction, integration and analytical absorption correction. Triangular shaped single crystals (Fig. 1) obtained from the reaction were used for the data collection.

2.4. Structural refinement

Indexing of all the reflections lead to a trigonal cell with the space group $P\bar{3}m1$. The direct method was used and the structure was refined using Shelxl-97 (full-matrix least-squares on F^2) [19] with anisotropic atomic displacement parameters for all atoms.

Table 1

Crystal data and structure refinement for $\text{YbGe}_{2.83}$ at 293(2) K.

Formula weight	378.29
Wavelength	0.71073 Å
Crystal system, space group	Trigonal, $P\bar{3}m1$
Unit cell dimensions	$a=8.3657(12)$ Å, $\alpha=90.00^\circ$ $b=8.3657(12)$ Å, $\beta=90.00^\circ$ $c=7.0469(14)$ Å, $\gamma=120.00^\circ$
Volume	$427.10(12)$ Å ³
Z, density (calculated)	4, 5.883 g/cm ³
Absorption coefficient	41.177 mm ⁻¹
$F(000)$	642
Crystal size	$150 \times 150 \times 150$ μm ³
Theta range for data collection	2.81 – 29.22°
Index ranges	$-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $-9 \leq l \leq 9$
Reflections collected	8016
Independent reflections	466 [$R_{\text{int}}=0.0790$]
Completeness to $\theta=29.22^\circ$	100%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	466/36/28
Goodness-of-fit on F^2	1.295
Final R indices [$> 2\sigma(I)$]	$R_{\text{obs}}=0.0483$, $wR_{\text{obs}}=0.0969$
Extinction coefficient	0.0023(3)
Largest diff. peak and hole	2.438 and -2.633 e Å ⁻³

$$R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \quad wR = \frac{\{\sum [w(|F_o|^2 - |F_c|^2)]^2\}^{1/2}}{\sum [w(|F_o|^4)]^{1/2}} \quad \text{and} \quad \text{calc } w = \frac{1}{[\sigma^2(F_o^2) + (0.0245P)^2 + 15.6684P]}, \quad \text{where } P = (F_o^2 + 2F_c^2)/3$$

As a check for the correct composition, the occupancy parameters were refined in a separate series of least-squares cycles. Initially, all sites were kept completely occupied, however, the refinement was largely unsatisfactory and marked with relatively high residuals ($R1 > 9\%$) and large thermal ellipsoids around the Ge2 atom ($U_{11}=U_{22}=0.66$ Å and $U_{33}=0.69$ Å). In order to avoid these, the Ge2 position was kept unoccupied and observed a pronounced decrease in the residuals ($R1=2.1$ Å) and thermal ellipsoids ($U_{11}=U_{22}=0.10$ Å and $U_{33}=0.13$ Å). This reduces the Ge2 atom occupancy to 42% in the 2d Wyckoff position. The initial crystallographic data showed some additional reflection along [100] and [010] directions suggesting the presence of a superstructure. In order to take those weak reflections into account, we repeated the data collection with increased exposure time and refined the structure successfully within same crystal system and space group but with doubling of a and b axes. In order to check the presence of In or Pd in the crystal structure, the germanium atoms at 2d (Ge1 and Ge3) and 6i (Ge2 and Ge4) positions were mixed with In and Pd in separate cycles and showed a slight rise in the equivalent isotropic displacement parameter indicated the absence of Ge/In and Ge/Pd mixing in $\text{YbGe}_{2.83}$. The details of the data collection and complete refinement are shown in Table 1. The atomic coordinates, anisotropic displacement parameters and interatomic distances are listed in Tables 2–4, respectively. Further information on the structure refinements is available.¹

2.5. Bond valence sum (BVS) calculations

Based on the Pauling's concept [20] the BVS surrounding the ytterbium atom is equal to the oxidation state z_{Yb} , as shown below

$$z_{\text{Yb}} = \sum S_{\text{YbGe}} \quad (1)$$

The valences of the individual bonds, S_{YbGe} in Eq. (1), can be calculated from the observed bond lengths using

$$S_{\text{YbGe}} = \exp[R_0 - R_{\text{YbGe}}]/b \quad (2)$$

¹ Details may be obtained from: Fachinformationszentrum Karlsruhe, Abt. PROKA, D-76344 Eggenstein-Leopoldshafen, Germany, by quoting the Registry no. CSD-421475.

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{YbGe}_{2.83}$ at 293(2) K with estimated standard deviations in parentheses.

Label	Wyckoff site	x	y	z	Occupancy	U_{eq}^a
Yb(1)	1a	0	0	0	1	4(1)
Yb(2)	3e	0	5000	0	1	1(1)
Ge(1)	2d	3333	6667	2580(3)	1	2(1)
Ge(2)	6i	1667(1)	8333(1)	7423(2)	1	2(1)
Ge(3)	2d	6667	3333	3551(7)	0.566(11)	4(1)
Ge(4)	6i	8334(3)	6669(6)	6275(5)	0.361(8)	6(2)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3

Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{YbGe}_{2.83}$ at 293(2) K with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Yb(1)	4(1)	4(1)	4(1)	2(1)	0	0
Yb(2)	1(1)	1(1)	1(1)	1(1)	0(1)	0(1)
Ge(1)	2(1)	2(1)	2(1)	1(1)	0	0
Ge(2)	2(1)	2(1)	2(1)	1(1)	0(1)	0(1)
Ge(3)	3(1)	3(1)	6(2)	2(1)	0	0
Ge(4)	6(2)	6(2)	5(2)	3(1)	0(1)	1(1)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^2U_{11} + \dots + 2hka^*b^*U_{12}]$.

Table 4

Bond lengths (\AA) for $\text{YbGe}_{2.83}$ at 293(2) K with estimated standard deviations in parentheses.

Label	Distance	Label	Distance
Yb(1)–Ge(2) $\times 6$	3.0219(13)	Ge(2)–Ge(4) $\times 2$	2.546(2)
Yb(1)–Ge(4) $\times 6$	3.566(4)	Ge(2)–Yb(2) $\times 2$	3.0217(10)
Yb(2)–Ge(2) $\times 4$	3.0217(10)	Ge(2)–Yb(1)	3.0219(13)
Yb(2)–Ge(1) $\times 2$	3.0230(14)	Ge(3)–Ge(2) $\times 3$	2.5103(19)
Yb(2)–Ge(3) $\times 2$	3.478(3)	Ge(3)–Ge(1)	2.726(5)
Yb(2)–Ge(4) $\times 4$	3.568(3)	Ge(3)–Yb(2) $\times 3$	3.477(3)
Ge(1)–Ge(4) $\times 3$	2.548(4)	Ge(4)–Ge(2) $\times 2$	2.546(2)
Ge(1)–Ge(3)	2.726(5)	Ge(4)–Ge(1)	2.548(4)
Ge(1)–Yb(2) $\times 2$	3.0230(14)	Ge(4)–Ge(2)	2.605(4)
Ge(2)–Ge(3)	2.5103(19)	Ge(4)–Yb(1)	3.566(4)
Ge(2)–Ge(4) $\times 2$	2.546(2)	Ge(4)–Yb(2) $\times 2$	3.568(3)
Ge(2)–Ge(4)	2.605(4)		

where R_{YbGe} is the observed bond length in $\text{YbGe}_{2.83}$, and R_0 is the constant dependent on the nature of YbGe pair. The constant b was determined to be 0.37 [21], which is a generally accepted value [22–25]. The R_0 value can be viewed as a bond length of unit valence. The usual procedure was to assume an oxidation state and to use a previously determined R_0 value appropriate to the bond being considered. The R_0 value was calculated using the software VALENCE [26] from the bond lengths and the oxidation state of YbAl_2Ge_2 [27]. The valences of Yb1 and Yb2 were calculated using the program CIFTOOL [28].

3. Results and discussion

3.1. Reaction chemistry

The combination of Yb, Ge and Pd or Ag in excess indium resulted in the formation of the new binary compound $\text{YbGe}_{2.83}$. We did not observe this new compound from similar stoichiometric reactions with other transition metals we studied such as Cr, Mn, Fe, Co, Ni, Cu, Ru and Au. Unfortunately, because of other

high thermodynamically stable Yb–Ge binaries it is difficult to synthesize the compound as a pure phase. Byproducts of these reactions include YbPd_2Ge_2 , Yb_4AgGe_8 , Yb_3Ge_5 and Yb_5Ge_3 and recrystallized germanium. The compound $\text{YbGe}_{2.83}$ crystallizes from indium flux as triangular shaped single crystals (Fig. 1). The crystals are stable in air for several months. At first we suspected that the transition metal may be incorporated into the structure to producing a ternary compound similar to the Yb–Si system where the inclusion of silver stabilizes the new compound $\text{YbAg}_{0.28}\text{Si}_{1.72}$ [29]. Therefore, we looked carefully at the possibility of transition metal or indium inclusion. Several EDS/SEM analyses systematically carried out on selected single crystals with long accumulation times of ~ 6 min did not indicate any transition metal present in the specimens (Fig. 1). Multiple measurements in different regions of the selected single crystals were also performed for better statistics (two of them are shown in Fig. 1) and clearly ruled out the presence of any detectable element other than Yb and Ge. Although the material does not form without a transition metal being present in the synthesis giving instead Yb_3Ge_5 and the ternary phases mentioned above, we speculate that the transition metals could act as a nucleating agents for the growth of $\text{YbGe}_{2.83}$ crystals. A similar such behavior was reported in the case of $\text{Yb}_5\text{Al}_2\text{Sb}_6$ [30].

The thermal stability and phase transformation of $\text{YbGe}_{2.83}$ were investigated. Pani and Palenzona [5] synthesized and refined the crystal structure of Yb_3Ge_8 ($\text{YbGe}_{2.67}$), which was close in composition to our compound, triclinic, but it is triclinic $P\bar{1}$ space group and crystallizes in its own structure type. They observed the formation of the compound at 865 °C. In order to check for any phase transition of $\text{YbGe}_{2.83}$ we annealed the sample up to 800 °C. We observed no change in the crystal structure of the compound but at 850 °C the single crystal decomposed completely and Ge melt formed.

Other synthetic techniques such as arc-melting, high frequency induction heating, direct heating in resistive furnaces also failed to produce the compound. Since $\text{YbGe}_{2.83}$ is the most germanium rich compound in the Yb–Ge system we also tried to grow crystals using germanium flux but were not successful.

3.2. Crystal structure

Crystal structure refinement shows that $\text{YbGe}_{2.83}$ is a germanium deficient variant superstructure of the CaAl_2Si_2 type [31] structure. The details of the data collection, complete refinement, the positional parameters and interatomic distances are listed in Tables 1–4. The evolution of $\text{YbGe}_{2.83}$ superstructure from CaAl_2Si_2 is shown in Fig. 2. In the substructure of $\text{YbGe}_{2.83}$, the Yb atom occupies the Ca position, while the Ge1 and Ge2 atoms occupy the Al and Si positions, respectively. The Yb and Ge1 sites are fully occupied while the Ge2 site is only 42% occupied. In the superstructure the a - and b -axis are doubled and every atom site splits into two different sites. Both the Yb and Ge1/Ge2 sites are fully occupied. The Ge3 and Ge4 sites are deficient but the degree of deficiency is different with 57% and 36%, respectively. Also two types of coordination environments are present for the Ge atoms: a flipped tetrahedron or umbrella shaped coordination for the Ge1 and Ge2 and a tetrahedron coordination for Ge3 and Ge4 atoms.

Fig. 3 shows the slabs of double puckered layers of fused Ge hexagons which stack along the c -axis to sandwich the Yb atom layers. The closest distance between the anionic germanium slabs is 4.4028(9) Å. $\text{YbGe}_{2.83}$ can be classified as a Zintl compound and can be written, more expressively, as $\text{Yb}^{(2+x)+}(\text{Ge}_2\text{Ge}_{2-x})^{(2+x)-}$. We separate the two different Ge sites in order to make a more direct comparison with its parent compound, CaAl_2Si_2 compound which is regarded as a Zintl phase [32]. In CaAl_2Si_2 the Al and Si atoms

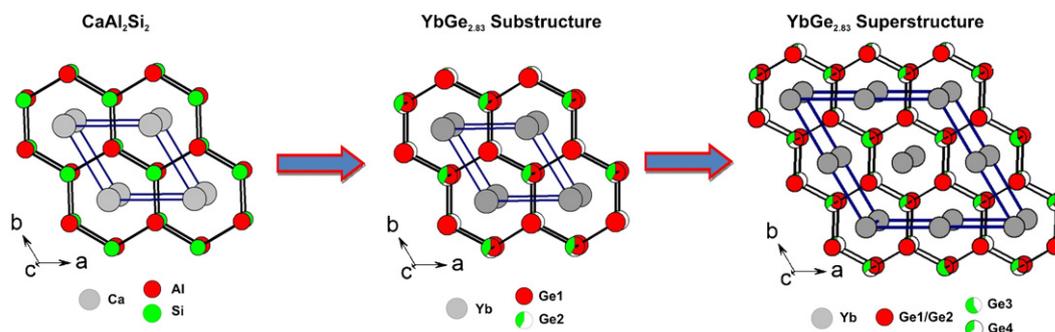


Fig. 2. Structural derivation of the superstructure of $\text{YbGe}_{2.83}$ from CaAl_2Si_2 through its substructure is shown. The unit cell is emphasized as blue lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

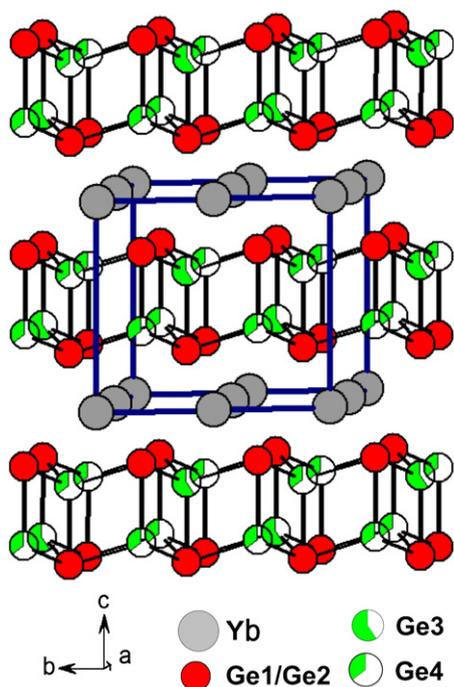


Fig. 3. Superstructure of $\text{YbGe}_{2.83}$ is shown along the a -axis. The unit cell is emphasized as blue lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

being 4-connected consistent with the formulation $\text{Ca}^{2+}(\text{Al}_2\text{Si}_2)^{2-}$. The two dimensional arrays of Yb ions are separated by tightly bound $(\text{Ge}_2\text{Ge}_{2-x})^{(2+x)-}$ layers (Fig. 3). It is expected that each atom in the Ge_4 layer is 4-connected and surrounded by other Ge atoms. However, Ge3 and Ge4 may exhibit 3-connected puckered nets as in the structure of α -As because of the deficiency at the Ge3 and Ge4 sites. The Zintl description requires that the ytterbium atoms either mixed or intermediate valent with an overall oxidation state of 2.35. Interestingly, except for Yb_3Ge_8 , all other Yb–Ge binaries were interpreted as classic Zintl phases [5]. Pani and Palenzona [5] indicated a probable mixed valence of Yb in those compounds based on the Zintl concept. So far, the experimental evidence for mixed valency is available only for Yb_3Ge_5 coming from the magnetic susceptibility and electrical resistivity measurements [33].

Valence bond sum (VBS) calculations for $\text{YbGe}_{2.83}$ were carried out to assess the oxidation state of the Yb ions. We used the isostructural compound YbAl_2Ge_2 [27] as standard for the estimation of R_0 because the divalent nature of Yb has been established from magnetic susceptibility measurements. The R_0

value was estimated at 2.618 using the program VALENCE [26] which for $\text{YbGe}_{2.83}$ indicated an oxidation state of 2.48 for Yb1 and 2.53 for Yb2 with an overall average value of 2.51. This is slightly higher than the postulated valence state using the Zintl concept ($\text{Yb}^{2.35+}$). This small increase in the Yb valence probably due to the defects at the germanium sites (Ge3 and Ge4) which were not taken into account for the VBS analysis.

The Yb–Ge distances of 3.0219(13) and 3.0217(10) Å in $\text{YbGe}_{2.83}$ are consistent with the $> +2$ oxidation state of the Yb atoms. By comparison, the shortest Yb–Ge distances in Yb_2Ge are 3.127(2) Å, in Yb_5Ge_3 2.899(2) Å, in Yb_5Ge_4 3.061(1) Å, in $\text{Yb}_{11}\text{Ge}_{10}$ 2.839(1) Å, in Yb_3Ge_5 3.030(1) Å, in Yb_3Ge_8 2.941(1) Å. This diversity in the bond distances is a consequence of the varying average oxidation state of Yb in these systems.

The average Ge1–Ge2 bond distances (2.5871 Å) in $\text{YbGe}_{2.83}$ are comparable with the Ge–Ge distances in other mixed valent compounds, e.g. Yb_3Ge_5 (2.576(1) Å) [5]. The bond length differences in CaAl_2Si_2 type Zintl compounds were discussed by Zheng et al. [32]. In comparison to that our compound shows different types of Ge–Ge distances in the $(\text{Ge}_4)^{2-}$ layers, the short one with 2.5103(19) Å and the large one with 2.726(5) Å. The nominal Ge zigzag chains of $\text{YbGe}_{2.83}$ are very similar to those in CaAl_2Si_2 in that the dihedral angles of the chains are 0°. The resulting Ge–Ge–Ge zigzag angles average at 111.23(7)° are pretty close to the corresponding angles in CaAl_2Si_2 , which are close to 112.104°.

4. Concluding remarks

$\text{YbGe}_{2.83}$ is a new binary compound in the Yb–Ge system obtained from indium flux. The crystal structure of $\text{YbGe}_{2.83}$ is a vacant variant of the CaAl_2Si_2 structure type and can be rationalized on the basis of the Zintl concept. The deficiency at the Ge sites and the Zintl phase description of $\text{YbGe}_{2.83}$ suggest an overall mixed/intermediate valence for Yb ($\text{Yb}^{+2.35}$).

Acknowledgments

Research supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award (Grant DE-FG02-07ER46356).

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