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Synthesis and Structure of YbCuGe and YbIrGe

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Summary. The equiatomic ytterbium–transition metal–germanides YbCuGe and YbIrGe were synthesized in single crystalline form from CuGe and IrGe master alloys and ytterbium *via* the *Bridgman* technique and they were characterized through their X-ray powder patterns. The structures were refined from X-ray single crystal diffractometer data: NdPtSb type, $P6_3mc$, $a = 421.36(8)$, $c = 703.9(1)$ pm, $wR2 = 0.0234$, 210 F^2 values, 11 variable parameters, BASF = 0.35(9) for YbCuGe and TiNiSi type, *Pnma*, $a = 671.09(6)$, $b = 421.55(5)$, $c = 757.16(7)$ pm, $wR2 = 0.0782$, 519 F^2 values, 20 variable parameters for YbIrGe. The copper (iridium) and germanium atoms build up [CuGe] and [IrGe] networks. In YbCuGe the two-dimensional [CuGe] network consists of puckered layers of Cu_3Ge_3 hexagons (247 pm Cu–Ge) that are charge balanced and separated by the ytterbium atoms. In contrast, the ordered Ir_3Ge_3 hexagons show a strong orthorhombic distortion and the [IrGe] network is three-dimensional with a distorted tetrahedral germanium coordination around iridium with almost equal Ir–Ge distances (252–259 pm). The ytterbium atoms fill cages within this network. The cell volumes of YbCuGe and YbIrGe are indicative for purely trivalent ytterbium.

Keywords. Ytterbium compounds; Crystal chemistry; Intermetallics.

Introduction

The ytterbium intermetallics Yb*TX* (*T* = transition metal; *X* = element of the 3rd, 4th, or 5th main group) have intensively been investigated in recent years with respect to their crystal chemistry and the largely varying physical properties. The many data have been summarized in a recent review [1, and Refs. therein]. Ytterbium displays an interesting situation in these intermetallics because of the interplay of divalent diamagnetic Yb^{2+} ([Xe] $4f^{14}$) and paramagnetic Yb^{3+} ([Xe] $4f^{13}$). Trivalent ytterbium compounds are particularly important for comparison

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Table 1. Lattice parameters of hexagonal YbCuGe (NdPtSb type, $P6_3mc$) and orthorhombic YbIrGe (TiNiSi type, *Pnma*); the values marked by an asterisk derive from the single crystals

Compound	a/pm	b/pm	c/pm	V/nm^3	Ref.
YbCuGe	418.60(3)	–	698.80(8)	0.1060	[3]
YbCuGe	421.3(1)	–	703.6(2)	0.1082	[4]
YbCuGe	421.9	–	704.9	0.1087	[19]
YbCuGe	421.36(8)	–	703.9(1)	0.1082	this work
YbCuGe*	421.43(7)	–	703.2(2)	0.1082	this work
YbIrGe	671.09(6)	421.55(5)	757.16(7)	0.2142	this work
YbIrGe*	670.6(1)	421.06(8)	757.1(2)	0.2138	this work

with cerium intermetallics, since they exhibit the *f*-hole analogon of [Xe] $4f^1$ cerium.

Most structures of the Yb*T*Ge germanides derive from the aristotype AlB_2 with an ordering of the transition metal and germanium atoms on the boron network [2]. The [*T*Ge] networks are often puckered and orthorhombically distorted. YbCuGe has so far only been characterized on the basis of X-ray powder data. *Dzyanyi* [3] and *Iandelli* [4] assigned the hexagonal $CaIn_2$ type to this germanide, however, they did not determine the ordering of copper and germanium. The lattice parameters showed some discrepancies (Table 1), indicative for a solid solution $YbCu_{1+x}Ge_{1-x}$ or $YbCu_{1-x}Ge_{1+x}$, similar to EuCuGe [5].

We have now obtained single crystals of YbCuGe *via* the *Bridgman* technique. These allowed a precise determination of the Cu–Ge-ordering. Additionally we determined the structure of the new germanide YbIrGe with TiNiSi type structure.

Results and Discussion

The structures of YbCuGe and YbIrGe have been refined from single crystal diffractometer data. The transition metal–germanium ordering was clearly determined

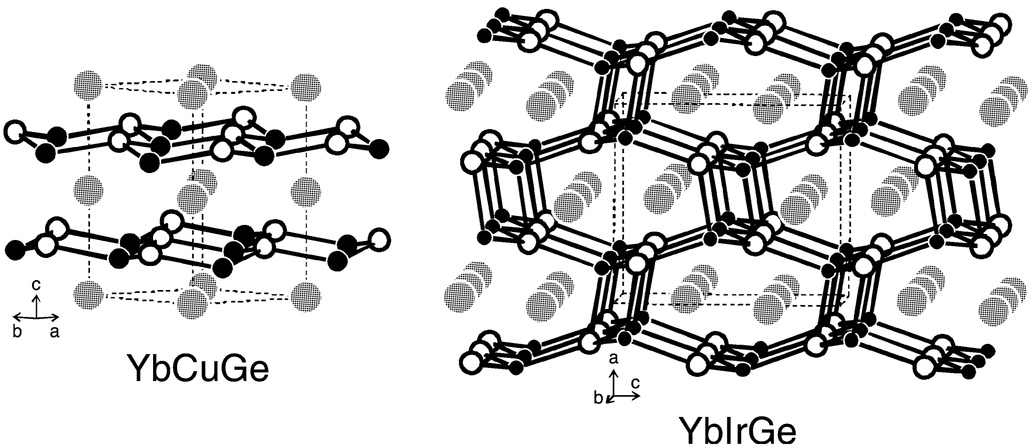

Fig. 1. Crystal structures of YbCuGe and YbIrGe; the ytterbium, copper (iridium), and germanium atoms are drawn as medium grey, filled, and open circles, respectively; the two-dimensional [CuGe] and the three-dimensional [IrGe] networks are emphasized

for both germanides. In Fig. 1 we present perspective views of the YbCuGe (NdPtSb type [15]) and YbIrGe (TiNiSi type [16]) structures. They derive both from the aristotype AlB_2 [2].

In YbCuGe the copper and germanium atoms build up ordered Cu_3Ge_3 hexagons with Cu–Ge distances of 247 pm, only slightly larger than the sum of the covalent radii of 239 pm [17]. The hexagonal networks are strongly puckered. They are rotated by 60° in every other layer. Due to the puckering the closest Cu–Ge distance between the layers is 307 pm, smaller than half the c axis (352 pm) which corresponds to the AlB_2 subcell. Nevertheless, the [CuGe] network is clearly two-dimensional. These networks are charge-balanced and separated by the ytterbium atoms. In the powder investigation by *Dzyanyi et al.*, the z parameter of the mixed occupied $4f$ Cu/Ge position, assuming the averaged $CaIn_2$ type in space group $P6_3/mmc$ [3], was $z = 0.218$ (with respect to Yb at $z = 0$). The well resolved Cu–Ge ordering results in different z values of 0.212 for Cu and 0.275 for Ge. These values differ by 0.038 (Cu) and 0.025 (Ge) from the ideal subcell (AlB_2 type) value of 1/4.

The puckering of the [IrGe] layers in YbIrGe is more pronounced (Fig. 1). Furthermore, the Ir_3Ge_3 hexagons show a strong orthorhombic distortion, leading to a three-dimensional [IrGe] network with Ir–Ge distances ranging from 252 to 259 pm, close to the sum of the covalent radii of 248 pm [17]. Thus, each iridium atom has four germanium neighbors in a strongly distorted tetrahedral coordination and *vice versa*. These $IrGe_{4/4}$ tetrahedra are condensed *via* all corners forming the three-dimensional network emphasized in Fig. 1. The ytterbium atoms fill larger cages left by this network. The stronger puckering and the orthorhombic distortion significantly influence the ytterbium coordination with respect to YbCuGe. In the copper compound each ytterbium atom has twelve nearest Cu/Ge neighbors, whereas in YbIrGe there are only eleven nearest Ir/Ge neighbors while the next germanium atom is already at an Yb–Ge distance of 354 pm. Furthermore, the strong puckering does not leave enough space for all ytterbium neighbors. From the $2 + 6$ neighbors in the slightly distorted hexagonal variant (YbCuGe), only six neighbors remain in YbIrGe. The two further ytterbium atoms are shifted away at the much longer Yb–Yb distance of 515 pm.

Finally we need to comment on the ytterbium valence in YbCuGe and YbIrGe. The course of the cell volumes within the series of *RE*CuGe and *RE*IrGe germanides [4, 8, 18] revealed no anomaly for the ytterbium compounds, indicating Yb^{III}. This is in good agreement with magnetic susceptibility measurements [4, 19, 20] which revealed experimental magnetic moments close to the free ion value of $4.54\,\mu_B$ for Yb^{3+}.

Experimental

Synthesis

YbCuGe and YbIrGe samples were prepared by the *Bridgman* method using sealed tungsten crucibles. The starting materials Yb, Cu, and Ir had a purity of 3N and Ge a purity of 4N. In a first stage CuGe and IrGe lumps were prepared beforehand by arc-melting under a purified argon atmosphere. Subsequently, stoichiometric amounts of an Yb lump and CuGe (IrGe) lumps were enclosed under vacuum in the crucibles. These crucibles were then heated up to 1260 and 1600 K for YbCuGe and YbIrGe, respectively. After keeping the crucibles at those temperatures for one hour, they were pulled down at a rate of 2 mm/h. The first YbIrGe crystals, however, originated from a sample of the starting composition 5Yb:Ir_4Ge_{10} using the same thermal treatment.

The YbCuGe and YbIrGe samples are very brittle and can easily be fragmented in a steel mortar. Compact pieces and powders are stable in air over long periods of time. Powders are dark gray; single crystals exhibit metallic luster.

The single crystals investigated on the four-circle diffractometer and the bulk samples have been analysed using a LEICA 420 I scanning electron microscope with YbF_3, Cu, Ir, and Ge as standards. No impurity elements heavier than sodium have been observed. The compositions determined by EDX were in good agreement with the ideal 1:1:1 composition.

X-Ray Film Data and Structure Refinements

Both samples were characterized through their *Guinier* powder patterns using $CuK_{\alpha 1}$ radiation and α-quartz ($a = 491.30$, $c = 540.46$ pm) as an internal standard. The *Guinier* camera was equipped with an imaging plate system (Fujifilm BAS-1800). The lattice parameters (Table 1) were obtained from least-squares fits of the *Guinier* data. To ensure correct indexing, the observed patterns were compared to calculated ones [6] using the atomic positions obtained from the structure refinements. The lattice parameters derived from the powders and the single crystals agreed well.

Table 2. Crystal data and structure refinement for YbCuGe (NdPtSb type, space group $P6_3mc$, Z = 2) and YbIrGe (TiNiSi type, space group *Pnma*, Z = 4)

Empirical formula	YbCuGe	YbIrGe
Molar mass	309.17 g/mol	437.83 g/mol
Unit cell dimensions	Table 1	Table 1
Calculated density	9.49 g/cm^3	13.58 g/cm^3
Crystal size	$15 \times 20 \times 40\ \mu m^3$	$10 \times 20 \times 40\ \mu m^3$
Transm. Ratio (max/min)	3.84	3.02
Absorption coefficient	65.9 mm^{-1}	118.7 mm^{-1}
$F(000)$	262	716
Detector distance	–	60 mm
Exposure time	–	3 min
ω range; increment	–	0–180°, 1.0°
Integr. parameters A, B, EMS	–	13.5; 3.5; 0.012
θ range	5–35°	4–35°
Range in *hkl*	±6, ±6, ±11	±10, ±6, ±12
Total no. reflections	1714	3028
Independent reflections	210 ($R_{int} = 0.0669$)	519 ($R_{int} = 0.1333$)
Reflections with $I > 2\sigma(I)$	184 ($R_\sigma = 0.0258$)	484 ($R_\sigma = 0.0693$)
Data/parameters	210/11	519/20
Goodness-of-fit on F^2	0.970	1.197
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0127$ $wR2 = 0.0225$	$R1 = 0.0334$ $wR2 = 0.0760$
R indices (all data)	$R1 = 0.0173$ $wR2 = 0.0234$	$R1 = 0.0381$ $wR2 = 0.0782$
BASF	0.35(9)	–
Extinction coefficient	0.041(2)	0.027(1)
Largest diff. peak and hole	0.64/−0.82 e/Å^3	4.64/−4.36 e/Å^3

Irregularly shaped single crystals of YbCuGe and YbIrGe were isolated from the larger blocks obtained by the *Bridgman* technique by mechanical fragmentation and first examined by *Laue* photographs on a *Buerger* precession camera (equipped with an imaging plate system Fujifilm BAS-1800) in order to establish suitability for intensity data collection. The data set for YbCuGe was collected at room temperature by use of a four-circle diffractometer (CAD4) with graphite monochromatized MoK$_\alpha$ ($\lambda = 71.073$ pm) radiation and a scintillation counter with pulse height discrimination. The scans were taken in the $\omega/2\theta$ mode. Intensity data of YbIrGe were recorded at room temperature by use of a *Stoe* IPDS-II diffractometer with graphite monochromatized MoK$_\alpha$ radiation. The absorption corrections for both crystals were numerical (X-Shape/X-Red). All relevant crystallographic data and details for the data collections and evaluations are listed in Table 2.

The isotypy of YbIrGe with the previously reported silicide YbIrSi [7] and LuIrGe [8] was already evident from the X-ray powder data. The extinctions conditions were compatible with space group *Pnma*. The atomic positions of LuIrGe [8] were taken as starting values and the structure was refined using SHELXL-97 (full-matrix least-squares on $F_o{}^2$) [9] with anisotropic atomic displacement parameters for all sites. As a check for the correct composition, the occupancy parameters were refined in a separate series of least-squares cycles. The sites are fully occupied within two standard deviations. In the last cycles, the ideal occupancies were assumed again.

Although the literature data did not reveal copper–germanium ordering for YbCuGe, we assumed this ordering for our starting model in a similar way as for CeAuGe [10] and CeAuSn [11]. The extinctions conditions were compatible with space group $P6_3mc$, in agreement with the results obtained for the cerium compounds. The starting positional parameters for YbCuGe were deduced from an automatic interpretation of direct methods with SHELXS-97 [12]. The z parameter of the ytterbium atoms was kept fixed at $z = 0$, since an automatic restraint of the floating origin was not possible due to the small number of parameters, similar to CeAuGe [10] and CeAuSn [11]. The refined *Flack* parameter [13, 14] indicated twinning by inversion. We then introduced the inversion twin matrix and refined the structure again, resulting in a twin ratio of 65:35. The twinning results from the *translationengleiche* symmetry reduction of index 2 (t2) ingoing from $P6_3/mmc$ to $P6_3mc$. The relatively large standard deviation of the batch scale factor certainly reflects the small difference in scattering power between copper and germanium. These elements differ only by three electrons. Refinement of the occupancy parameters also underlined the copper–germanium ordering for YbCuGe.

Final difference *Fourier* synthesis revealed no significant residual peaks (see Table 2) for YbCuGe. The highest residual peaks for YbIrGe were close to the iridium sites (76 pm) and most likely resulted from an incomplete absorption correction of this strongly absorbing compound. The positional parameters and interatomic distances of both refinements are listed in Tables 3 and 4. Further details on the

Table 3. Atomic coordinates and anisotropic displacement parameters (pm^2) for YbCuGe and YbIrGe; U_{eq} is defined as a third of the trace of the orthogonalized U_{ij} tensor; the anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + \cdots + 2hka^*b^*U_{12}]$; $U_{23} = 0$; the z parameter of Yb in YbCuGe was fixed at 0

Atom	*Wyckoff* site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{eq}
YbCuGe (space group $P6_3mc$)										
Yb	2*a*	0	0	0	92(1)	U_{11}	60(1)	46(1)	0	81(1)
Cu	2*b*	1/3	2/3	0.712(1)	71(12)	U_{11}	208(25)	35(6)	0	117(10)
Ge	2*b*	1/3	2/3	0.275(1)	73(9)	U_{11}	112(16)	37(5)	0	86(6)
YbIrGe (space group *Pnma*)										
Yb	4*c*	0.99007(8)	1/4	0.68997(7)	43(3)	53(2)	31(3)	0	8(2)	43(2)
Ir	4*c*	0.33885(7)	1/4	0.43805(6)	50(3)	49(2)	36(3)	0	6(1)	45(2)
Ge	4*c*	0.2106(2)	1/4	0.1148(2)	33(5)	37(5)	42(6)	0	7(5)	37(3)

Table 4. Interatomic distances (pm) in the structures of YbCuGe and YbIrGe, calculated with the lattice parameters taken from X-ray powder data; standard deviations are given in parenthesis

YbCuGe				YbIrGe				YbIrGe			
Yb:	3	Cu	285.3(4)	Yb:	2	Ge	290.5(1)	Ir:	2	Ge	251.9(1)
	3	Ge	290.2(4)		2	Ge	296.7(1)		1	Ge	252.3(1)
	3	Ge	311.0(5)		1	Ge	297.4(2)		1	Ge	259.4(2)
	3	Cu	316.7(5)		1	Ir	299.4(1)		1	Yb	299.4(1)
	2	Yb	352.0(1)		1	Ir	301.9(1)		1	Yb	301.9(1)
	6	Yb	421.4(1)		2	Ir	304.8(1)		2	Yb	304.8(1)
Cu:	3	Ge	247.3(1)		2	Ir	320.2(1)		2	Ir	316.3(1)
	3	Yb	285.3(4)		2	Yb	347.6(1)		2	Yb	320.2(1)
	1	Ge	307.3(2)		1	Ge	354.1(2)	Ge:	2	Ir	251.9(1)
	3	Yb	316.7(5)		2	Yb	356.9(1)		1	Ir	252.7(1)
Ge:	3	Cu	247.3(1)		2	Yb	421.6(1)		1	Ir	259.4(2)
	3	Yb	290.2(4)						2	Yb	290.5(1)
	1	Cu	307.3(2)						2	Yb	296.7(1)
	3	Yb	311.0(5)						1	Yb	297.4(2)

structure refinements may be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry Nos CSD-414432 (YbCuGe), and CSD-414433 (YbIrGe).

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