Crystal structure of DyAg$_{\sim 3}$In$_3$

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The DyAg$_{\sim 3}$In$_3$ compound was prepared by arc-melting of pure compact metals under an argon atmosphere. The crystal structure was refined from synchrotron powder diffraction data (space group *Im*-3, a = 15.1472(2) Å, Z = 24, R_p = 0.0792, R_{wp} = 0.1031, R_{exp} = 0.0231, refined composition DyAg$_{3.010}$In$_3$) and from conventional X-ray single crystal diffraction data (a = 15.1010(1) Å, R = 0.0423, R_w = 0.0433, refined composition DyAg$_{2.853}$In$_3$). The crystal structure belongs to the YbAg$_2$In$_4$ structure type, which is closely related to the structures of YbCd$_6$ and YCd$_6$.

1. Introduction

Ternary compounds of rare-earth metals (*RE*) with 3*d*-metals and indium have recently attracted the attention of researchers, due to their interesting physical, mainly magnetic and electrical, properties [1]. The corresponding systems with 4*d*-, 5*d*- and noble metals are less studied, but several papers dedicated to them and their compounds have appeared the last years [2-11].

In an earlier examination of the Yb–Ag–In system, the existence of the YbAg$_2$In$_4$ compound, which crystallizes in its own structure type, was discovered and its crystal structure and physical properties were investigated [12]. The compound has a relatively complex structure with a large lattice constant (a = 15.324 Å). The structure is defective with silver atoms occupying split-positions and is closely related to the binary intermetallides YCd$_6$ [13] and YbCd$_6$ [14]. A comparative analysis of the crystal structures of these compounds can be found in [12]. New representatives of the structure type are described in [15-18]. Phases with local pseudoicosahedral structure were found at the composition *RE*$_{16}$Ag$_{42}$In$_{42}$ (*RE* = Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) in [17]. Thermal and electrical properties of quasicrystals of the Yb–Ag–In system were studied in [18]. An X-ray single crystal investigation of the TbAg$_3$In$_3$ compound, isostructural with YbAg$_2$In$_4$, was

performed in [19]. Formation of similar compounds has been revealed in several *RE*–Ag–In systems (*RE* = Ce, Pr, Eu, Gd, Tb, Dy, Er, Tm) [20] and an X-ray diffraction analysis of complex metallic alloys has been carried out for the Eu–Ag–In system [21]. Recently, a new series of *RE*Pd$_2$In$_4$ compounds (*RE* = Sm, Gd-Ho) with YbAg$_2$In$_4$ structure type was found [22].

During an investigation of the phase equilibria in the Dy–Ag–In system at 870 K the existence of a ternary compound of composition DyAg$_{\sim 3}$In$_3$ was confirmed. The determination of the crystal structure of this compound by means of conventional X-ray single crystal diffraction and synchrotron powder diffraction is the object of this work.

2. Experimental

Samples for the investigation were prepared by arc melting under an argon atmosphere (purified with a titanium getter) from compact metals of high purity: Dy 99.8 wt.%, Ag 99.98 wt.%, and In 99.999 wt.%. Homogeneous annealing was performed at 870 K for one month. High-resolution powder diffraction data were collected for an annealed alloy of composition Dy$_{15}$Ag$_{43}$In$_{42}$ at room temperature (0.5 mm glass capillary). Synchrotron radiation (Materials Science Beamline at the SLS, PSI; silicon strip detector

Table 1 Experimental and crystallographic data for DyAg$_{~3}$In$_3$.

	Synchrotron X-ray powder diffraction [a]	X-ray single crystal diffraction
Composition	DyAg$_{3.010}$In$_3$	DyAg$_{2.853}$In$_3$
Mr, g mol^{-1}	831.634	814.701
Structure type	YbAg$_2$In$_4$	YbAg$_2$In$_4$
Space group	*Im*-3 (204)	*Im*-3 (204)
Z; Pearson code	24; *cI*168.240	24; *cI*164.472
Lattice parameter, Å	a = 15.1472(2)	a = 15.1010(1)
Cell volume, Å^3	3475.3(2)	3443.64(7)
Crystal size, μm^3	–	~120×80×15
Color	metallic dark gray	metallic dark gray
Calculated density, g cm^{-3}	9.5438(4)	9.4238(2)
Radiation type; wavelength, Å	synchrotron; 0.49063	Mo Kα; 0.71073
Absorption coefficient, mm^{-1}	383.49	341.33
Range in *hkl*	–	$-19 \leq h \leq 22$ $-22 \leq k \leq 23$ $-23 \leq l \leq 22$
Reflections collected/unique	–	1159/791
$2\theta_{min}$-$2\theta_{max}$, deg.	2.59-76.89	6.60-65.74
Refinement method	full profile	full-matrix least-squares
Refined parameters	65	44
Goodness-of-fit on F^2	–	1.06
Final R indices [I>2sigma(I)]	R_p = 0.0792, R_{wp} = 0.1031 R_B = 0.178	R_I = 0.0423, R_w = 0.0433

[a] Impurities: 2 – DyIn$_3$ phase (18.92 wt.%, AuCu$_3$-type, space group *Pm*-3*m*, a = 4.5364(2) Å), 3 – Ag$_7$In$_3$ phase (2.73 wt.%, Mg-type, space group *P*6$_3$/*mmc*, a = 3.0044(4), c = 4.7668(4) Å).

MYTHEN II) with a wavelength of λ = 0.49063 Å was used. The diffractometer was calibrated with an external silicon standard.

A single crystal of irregular shape was selected mechanically from the same alloy. Single crystal diffraction data were collected on an Xcalibur 3 diffractometer (Oxford Diffraction) equipped with a monochromatic Mo Kα source (λ = 0.71073 Å). The exposure time was 80 s per frame. The collection of intensity data was carried out with the CrysAlis program. The final lattice parameters were calculated from all the observed reflections in the actual data collection. The structure was solved by direct methods, and refined by using the WinCSD program package [23]. The crystallographic data and details of the data collection are listed in Table 1.

The single crystal investigated on the diffractometer was also studied by energy-dispersive X-ray analysis (EDX), using a Leica420i scanning electron microscope.

3. Results and discussion

Based on the results of the phase analysis of the alloys of Dy–Ag–In system, the composition of the investigated compound was found to be *RE*Ag$_{~3}$In$_3$, as for the TbAg$_3$In$_3$ compound [19]. The composition was confirmed by EDX analysis of the surface of the single crystal. Experimental data and the results of the X-ray synchrotron powder diffraction analysis (Fig. 1)

and the X-ray (Mo K$_\alpha$) single crystal diffraction analysis are shown in Table 1. It should be noted that the powder specimen contained small amounts of DyIn$_3$ (18.92 wt.%) [24] and Ag$_7$In$_3$ (2.73 wt.%) [25] (Fig. 1). The refined unit cell parameters determined from the synchrotron powder diffraction data (15.1472(2) Å) agree well with the values reported in [17] (15.17 Å) for an alloy of composition Dy$_{16}$Ag$_{42}$In$_{42}$ (conventional X-ray powder diffraction data), but are slightly higher than those obtained from the single crystal data (15.1010(1) Å). This indicates the possible existence of a small homogeneity range. Testing of various models based on both single crystal and powder diffraction data allowed us to assign the YbAg$_2$In$_4$ structure type (space group *Im*-3) to the DyAg$_{~3}$In$_3$ compound. The basic structure motif of these compounds is the same. However, part of the Wyckoff positions (12*e* and 12*d*) that are occupied by In atoms in the structure of YbAg$_2$In$_4$ are in the DyAg$_{~3}$In$_3$ compound occupied by Ag atoms (Ag6, Ag7). This model (Table 2) yields lower reliability factors and more regular values of the thermal parameters, both in the isotropic (Table 2) and anisotropic approximations (Table 3). The atomic coordinates refined for Dy and In agree well for powder and single crystal data and correspond well to the respective parameters in TbAg$_3$In$_3$. The positional parameters and the site occupancy ($\approx$1) of the atoms Ag6 and Ag7 (Table 2) are practically the same for the Dy- (both powder and single crystal data) and Tb-compounds. The site

Table 2 Atomic coordinates and isotropic displacement parameters for DyAg$_{3.010}$In$_3$ (synchrotron X-ray powder data – [1]first row), DyAg$_{2.853}$In$_3$ (conventional X-ray single crystal data – [2]second row) and TbAg$_3$In$_3$ (conventional X-ray single crystal data [19] – [3]third row). Space group *Im*-3.

Atom	Wyckoff position	Occ.	x	y	z	B_{iso}, Å^2
[1]Dy	24*g*	1	0	0.1868(2)	0.3032(2)	0.39(9)
[2]Dy	24*g*	1	0	0.18611(9)	0.3030(1)	0.94(3)
[3]Tb	24*g*	1	0	0.19692(3)	0.31391(3)	–
[1]Ag1,2	16*f*	1	0.1605(2)	0.1605(2)	0.1605(2)	2.32(9)
[2]Ag1,2	16*f*	0.93(1)	0.1624(2)	0.1624(2)	0.1624(2)	1.87(4)
[3]Ag1	16*f*	0.67(3)	0.1652(3)	0.1652(3)	0.1652(3)	–
[3]Ag2	16*f*	0.33(3)	0.1515(6)	0.1515(6)	0.1515(6)	–
[1]Ag3	24*g*	0.76(2)	0	0.2380(4)	0.0906(3)	1.2(2)
[1]Ag4	24*g*	0.13(2)	0	0.286(2)	0.083(2)	1.6(14)
[2]Ag3	24*g*	0.749(3)	0	0.2469(3)	0.0938(3)	1.51(9)
[2]Ag4	24*g*	0.206(4)	0	0.2224(11)	0.0873(15)	0.91(7)
[3]Ag3	24*g*	0.61(2)	0	0.2507(4)	0.0954(7)	–
[3]Ag4	24*g*	0.40(2)	0	0.2273(6)	0.0875(1)	–
[1]Ag5	48*h*	0.15(2)	0.0808(15)	0.0569(12)	0.1092(11)	1.9(8)
[2]Ag5	48*h*	0.086(1)	0.0904(11)	0.0172(10)	0.0722(11)	0.75(11)
[2]Ag5'	48*h*	0.053(3)	0.091(2)	0.055(3)	0.054(2)	1.1(4)
[3]Ag5	48*h*	0.16(1)	0.0892(5)	0.0254(6)	0.0638(1)	–
[1]Ag6	12*e*	1	0.1975(4)	0	½	1.8(3)
[2]Ag6	12*e*	1	0.1911(2)	0	½	1.20(7)
[3]Ag6	12*e*	1	0.19237(7)	0	½	–
[1]Ag7	12*d*	1	0.4092(4)	0	0	1.3(2)
[2]Ag7	12*d*	1	0.4094(3)	0	0	1.72(8)
[3]Ag7	12*d*	1	0.40988(8)	0	0	–
[1]Ag8	12*d*	0.29(2)	0	0	0.2007(12)	1.4(13)
[2]	–	–	–	–	–	–
[3]	–	–	–	–	–	–
[1]In1	24*g*	1	0	0.3998(3)	0.3477(3)	1.6(2)
[2]In1	24*g*	1	0	0.4025(2)	0.3462(2)	1.40(5)
[3]In1	24*g*	1	0	0.40263(5)	0.34672(5)	–
[1]In2	48*h*	1	0.2006(2)	0.1180(2)	0.3372(2)	1.58(11)
[2]In2	48*h*	1	0.2026(1)	0.1177(1)	0.3398(1)	1.73(4)
[3]In2	48*h*	1	0.20274(4)	0.11760(4)	0.33970(4)	–

splitting is typical for the Ag3,4 atoms for both compounds, however for the Tb compound the total occupancy was equal to 1, whereas for the Dy compound it is slightly lower (0.89 for the powder diffraction data and 0.96 for the single crystal data). Only the refinement on single crystal diffraction data show site splitting for the Ag5 (Ag5') atoms for the DyAg$_{\sim 3}$In$_3$ compound, but the site occupancy 0.14 agrees well with the results obtained by X-ray powder diffraction and with the results for TbAg$_3$In$_3$. Another difference is observed for the 16*f* position occupied by Ag1 atoms, which is split in the case of TbAg$_3$In$_3$, whereas splitting is not observed by either structure

determination method for the DyAg$_{\sim 3}$In$_3$ compound. The powder diffraction analysis yielded a site occupancy less than 1 for DyAg$_{\sim 3}$In$_3$. Finally, an additional atom site was located based on the X-ray powder analysis: Ag8 in Wyckoff position 12*d* with occupancy factor 0.29.

The refinement of the crystal structure resulted in the composition DyAg$_{3.010}$In$_3$ for the powder diffraction data and DyAg$_{2.853}$In$_3$ for the single crystal data. The small deficiency in silver atoms found for the single crystal led to lower values of the cell parameters. Interatomic distances and coordination numbers of the atoms are presented in Table 4.

Table 3 Anisotropic displacement parameters (Å^2) for DyAg$_{3.010}$In$_3$ (synchrotron X-ray powder diffraction) and DyAg$_{2.853}$In$_3$ (conventional X-ray single crystal diffraction).

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
			DyAg$_{3.010}$In$_3$			
Dy	0.49(15)	0.37(14)	0.3(2)	0	0	-0.17(13)
Ag1,2	2.32(15)	2.32(15)	2.32(15)	0.4(2)	0.4(2)	0.4(2)
Ag3,4	1.1(4)	1.5(4)	0.9(4)	0	0	0.4(3)
Ag6	2.2(4)	1.4(4)	2.0(4)	0	0	0
Ag7	1.0(4)	1.5(4)	1.5(4)	0	0	0
In1	1.6(3)	1.4(3)	1.9(3)	0	0	-0.4(2)
In2	1.3(2)	1.9(2)	1.5(2)	0.3(2)	-0.19(14)	-0.3(2)
			DyAg$_{2.853}$In$_3$			
Dy	0.86(5)	0.88(4)	1.08(5)	0	0	-0.06(4)
Ag1,2	1.87(6)	1.87(6)	1.87(6)	1.29(8)	1.29(8)	1.29(8)
Ag3,4	0.90(10)	2.6(2)	1.03(12)	0	0	0.6(2)
Ag6	0.86(11)	0.92(11)	1.82(12)	0	0	0
Ag7	1.13(12)	2.9(2)	1.19(12)	0	0	0
In1	1.48(8)	1.38(8)	1.33(8)	0	0	0.04(6)
In2	1.46(6)	2.38(7)	1.37(5)	0.60(5)	-0.35(5)	-0.43(5)
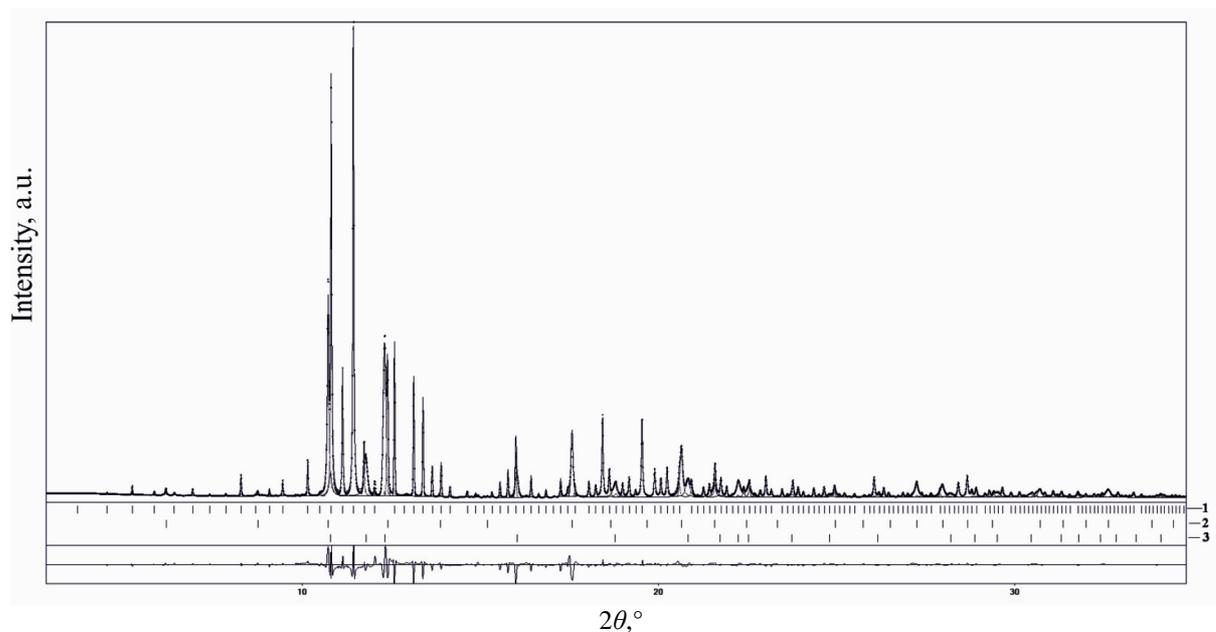
Fig. 1 Observed (circles), calculated (solid line) and difference diffraction patterns of the Dy$_{15}$Ag$_{43}$In$_{42}$ alloy: 1 – DyAg$_{3.010}$In$_3$; 2 – DyIn$_3$; 3 – Ag$_7$In$_3$. Synchrotron radiation, $\lambda = 0.49063$ Å.

The interatomic distances Ag-Ag within the coordination polyhedra range from 2.46 (Ag4-Ag5) to 3.19 Å (Ag6-Ag7), *i.e.* approximately 11 % less and more than the sum of the atomic radii, respectively. The shortest distance In-In is 2.86 Å (In2-In2) and the longest one is 3.56 Å (In2-In2), *i.e.* also 10-12 % less and more than the sum of the atomic radii [26]. The coordination polyhedra of the Dy atoms (CN = 16) is a pentagonal prism with additional atoms capping all of the lateral faces and one base. The coordination numbers of the Ag atoms are 10 for Ag1-Ag4, 7 for Ag5, 12 for Ag6, and 11 for Ag7, and correspond to coordination polyhedra in the form of trigonal prisms and derivatives of icosahedrons. The indium atoms have slightly higher coordination numbers, 12 for In1 and In2 (Fig. 2).

4. Conclusions

Quasicrystals are extremely sensitive to different external influences (*e.g.* temperature). In the YbCd$_6$ compound, one of the Cd atoms (Cd2) occupies the position 24*g* with occupancy 1/3 at 90 K, but 48*h* with

Table 4 Interatomic distances (δ, Å) and coordination numbers (CN) of the atoms in DyAg$_{2.853}$In$_3$.

| Atom		δ, Å	CN	Atom		δ, Å	CN	Atom		δ, Å	CN
Dy	2In2	3.180(2)	16	Ag4	1Ag5	2.46(4)	10	Ag7	1Ag7	2.736(5)	11
	1Ag7	3.237(2)		(or	1Ag5	2.58(3))			2Ag1,2	2.833(5)	
	2Ag3	3.259(3)		(or	1Ag5	2.81(3))			4In1	3.071(3)	
(or	2Ag4	3.303(2))			1Ag4	2.73(2)			2Ag6	3.194(3)	
	2Ag1,2	3.264(3)		(or	1Ag3	2.77(2))			2Dy	3.237(2)	
	2In2	3.277(2)			2Ag1,2	3.06(2)		In1	1Ag6	2.719(3)	12
	1Ag1,2	3.290(5)			2In2	3.029(11)			1Ag6	2.766(4)	
	2In2	3.293(2)			1Ag7	3.077(11)			1In1	2.943(3)	
	1In1	3.333(3)			2Dy	3.65(2)			2In2	2.945(2)	
	2In1	3.355(2)			1Dy	3.65(2)			2In2	2.959(3)	
	1Ag6	3.506(2)		Ag5	1Ag4	2.81(3)	7		2Ag7	3.071(3)	
Ag1,2	2In2	2.798(4)	10	(or	1Ag3	2.92(4))			1Dy	3.333(3)	
	2Ag5	2.56(3)			1Ag4	2.58(3)			2Dy	3.355(2)	
	1Ag7	2.833(5)		(or	1Ag3	2.92(4))		In2	1Ag1,2	2.798(4)	12
	2Ag4	2.65(2)			1Ag1,2	2.56(3)			1Ag8	2.828(3)	
(or	2Ag3	2.76(2))			2Ag5	2.79(19)			2In2	2.861(3)	
	2Dy	3.2595(3)		(or	2Ag5	3.10(4))			1In1	2.945(2)	
	1Dy	3.290(5)		(or	1Ag5	2.74(4))			1In1	2.959(3)	
Ag3	2In2	2.869(5)	10	(or	1Ag5	3.19(4))			1Ag6	3.007(2)	
	1Ag4	2.73(3)		(or	2Ag5	3.21(4))			1Dy	3.180(2)	
(or	1Ag3	2.744(7))		(or	2Ag5	3.39(4))			1Dy	3.277(2)	
	1Ag7	3.12(2)		(or	1Ag5	3.52(4))			1Dy	3.293(2)	
	1Ag5	2.92(4)		(or	1Ag5	3.58(4))			1In2	3.555(3)	
(or	1Ag5	3.04(4))			1Ag4	2.96(3)			1Ag7	3.567(2)	
(or	1Ag5	3.36(2))		(or	1Ag3	3.04(4))					
	2Ag1,2	2.76(2)			1Ag1,2	3.03(3)					
	2Dy	3.334(11)		Ag6	2In1	2.719(3)	12				
	1Dy	3.30(2)			2In1	2.766(4)					
					4In2	3.007(2)					
					2Ag7	3.194(3)					
					2Dy	3.506(2)					
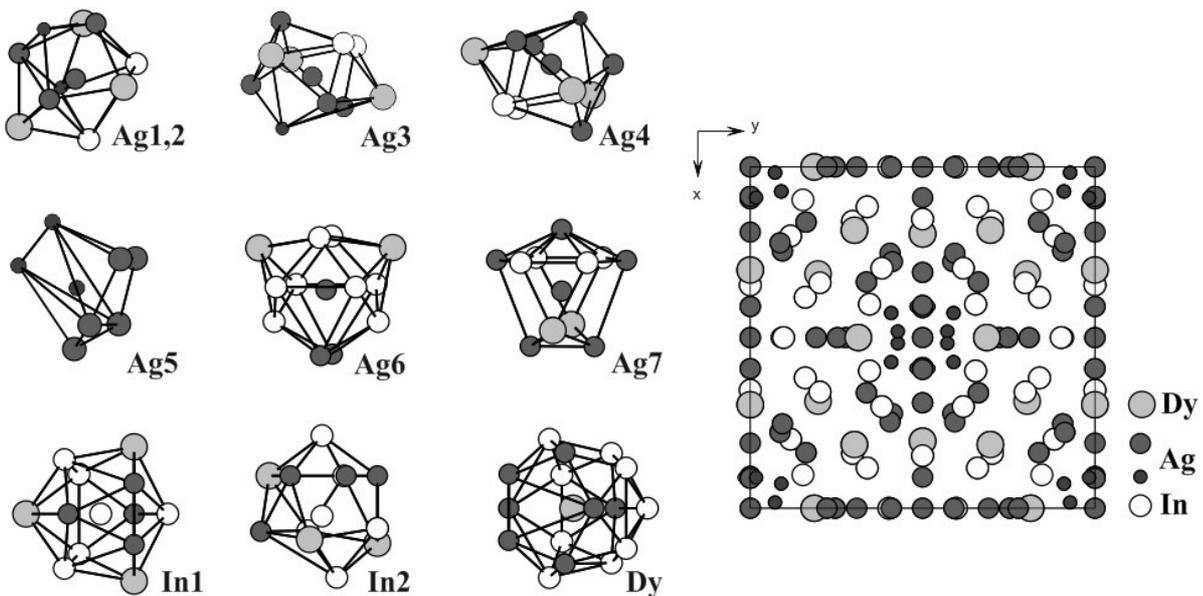
Fig. 2 Projection of the crystal structure of DyAg$_{2.853}$In$_3$ and the coordination polyhedra of the atoms (from X-ray single crystal diffraction data).

occupancy 1/6 at 240 K [27]. Similar changes are observed for other *RE*Cd$_6$ compounds, especially when *RE* = Pr, Eu. In this case both the splitting of the atomic positions and their occupancies change [28]. Similar differences exist between the structures of YbAg$_2$In$_4$ [12], TbAg$_3$In$_3$ [19] and DyAg$_{3.010}$In$_3$ (or DyAg$_{2.853}$In$_3$), although the basic structural motif remains unchanged.

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