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Crystal structures and magnetism of $DyAl_xGa_{3-x}$ (where $x = 0.33$ and $x = 0.85$)

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ABSTRACT

New ternary compounds have been obtained from arc-melting of the elements. The crystal structures have been investigated by powder X-ray diffraction analysis. $DyAl_{0.33}Ga_{2.67}$ crystallizes in space group $P6_3/mmc$ ($a = 6.1649(1)$ Å, $c = 23.0792(1)$ Å) with $Ta(Rh_{0.33}Pd_{0.67})_3$-type structure. The structure of $DyAl_{0.85}Ga_{2.15}$ has been refined with rhombohedral symmetry (space group $R\text{-}3m$, $a = 6.1702(1)$ Å, $c = 20.7797(1)$ Å), $BaPb_3$-type structure. The structures of the compounds have been analyzed crystallographically and the structural relationship has been established. Heat capacity measurements prove antiferromagnetic ordering at Néel temperatures of 12.6(1) K for $DyAl_{0.33}Ga_{2.67}$ and 10.0(1) K for $DyAl_{0.85}Ga_{2.15}$.

1. Introduction

Rare-earth based compounds are an interesting subject of research due to their widespread potential applications such as permanent magnets [1], magnetocaloric systems [2], hydrogen storage materials [3] and other applications.

A literature review of binary rare-earth-metal systems attracted our attention to the Dy–Ga and Al–Dy systems, namely to the binary compounds $DyGa_3$ and $DyAl_3$ which crystallize in numerous polymorphic modifications with closely related structures. According to the Massalski compilation of binary phase diagrams [4], $DyGa_3$ undergoes two temperature-induced polymorphic modifications. The ht2-$DyGa_3$ phase crystallize in the $AuCu_3$ structure type (1045 °C–550 °C), the ht1-$DyGa_3$ modification adopts the $Ta(Rh_{0.33}Pd_{0.67})_3$ structure type (550 °C–350 °C) and the rt-$DyGa_3$ phase crystallizes in the Mg_3In structure type (below 350 °C). Dysprosium trialuminide is characterized by the existence of two modifications: the $TiNi_3$-type one which is stable up to 1005 °C, and a $HoAl_3$-type (1005–1090 °C) one [4]. A high pressure $AuCu_3$-type modification is also formed [5]. Metastable $PuGa_3$ and $BaPb_3$ polymorphs obtained by rapid solidification, were reported in Ref. [6].

Shifting of phase transition temperatures and/or the stabilization of metastable phases with corresponding changes in physical properties is interesting both from theoretical and practical points of view. Such possibilities were demonstrated in Refs. [7–9] and a significant influence on the magnetic properties was achieved by substitution of a small amount of a nonmagnetic element.

Based on previous results and a literature review, a hypothesis that an isoelectronic Al/Ga atoms replacement ($r(Al)_{at.} = 1.431$, $r(Al)_{at.} = 1.221$, difference in atomic radii ~15% [10]) may have a stabilizing effect was made.

In this work we present results of investigations of the pseudo-binary system $DyGa_3$–$DyAl_3$, including crystallographic peculiarities of new phases and their magnetic susceptibilities.

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2. Experimental details

2.1. Synthesis and structural analysis

For the investigation of the pseudo-binary system $DyGa_3$–$DyAl_3$ nine samples were prepared from elemental Dy (99.95%), Al (99.999%) and Ga (99.99%). During the arc-melting procedure, titanium was heated prior to the melting of the reactant mixtures to further purify the argon atmosphere. The buttons were flipped over several times and remelted to achieve high homogeneity, then weighed back in order to check for possible mass losses. No significant mass loss (more than 1%) was found. The samples were then wrapped in Ta foil, sealed in evacuated fused silica capsules, and annealed at 870 K for 10 days and subsequently quenched in water. The crystal structures of the ternary compounds were refined by the Rietveld method using X-ray powder diffraction data collected on a Guinier Huber G 670 ($CuK\alpha_1$ radiation) machine. All procedures including indexing, refinement of the profile and structural parameters as well as calculations of interatomic distances were performed with the WINCSD [11] program package.

2.2. Magnetic measurements

Magnetic and heat capacity investigations have been performed for the two samples $Dy_{25}Al_{10}Ga_{65}$ ($Ta(Rh_{0.33}Pd_{0.67}$-type structure)) and $Dy_{25}Al_{20}Ga_{55}$ ($BaPb_3$-type structure). The measurements were carried out on a Quantum Design Physical Property Measurement System using the Vibrating Sample Magnetometer and the Heat Capacity option, respectively. For the magnetic (heat capacity) measurements 15.033 (4.278) mg of $Dy_{25}Al_{10}Ga_{65}$ and 17.061 (7.987) mg of $Dy_{25}Al_{20}Ga_{55}$ were used. These small pieces obtained from bulk materials were attached to the sample holder rod by kapton foil. For the heat capacity measurements, the pieces were fixed to a pre-calibrated heat capacity puck using Apiezon N grease. Magnetic investigations were performed in the temperature range of 2.5–300 K with a magnetic flux density up to 80 kOe and heat capacity measurements in the range of 2–300 K.

3. Results and discussion

3.1. Structure determination and refinement

After the substitution of 5 atomic per cent of aluminium by gallium atoms in $DyAl_3$, the diffraction pattern showed the presence of the $DyAl_3$ phase ($TiNi_3$-type) together with a new secondary phase. During further substitution (10%) no $TiNi_3$-type phase was observed.

After powder data indexing of the $Dy_{25}Al_{65}Ga_{10}$ sample, the $BaPb_3$ structure type was taken as an initial model, no additional un-indexed peaks could be observed. The phase with this type remains stable up to 55 at. % Ga. Since aluminium and gallium are p^1-elements and they have related chemical nature, Ga/Al (X) statistical mixtures were set in the initial model and the structure was successfully refined. The main crystallographic data were standardized by the STRUCTURE TIDY program [12] and the results of the Rietveld refinement of the $Dy_{25}Al_{20}Ga_{55}$ ($DyAl_{0.8}Ga_{2.2}$) sample are summarized in Tables 1, 2 and 4. Graphical representation is shown on Fig. 1a. Other tested derivative models did not yield a successful refinement. No significant changes of the unit cell volumes in the solid solution ($BaPb_3$-type) were observed, lattice parameters are represented in Table 5. Therefore the packing efficiencies (p.e.) (p.e. = (volume of atoms/volume of unit cell) × 100%) for the extreme solid solution composition were calculated. It was found that the p.e. for the $Dy_{25}Al_{10}Ga_{65}$ phase is 77% and 66% for the $Dy_{25}Al_{20}Ga_{55}$ phase which explains the constant unit cell volume during the Ga/Al substitution.

Table 1
Structural data and crystallographic data recording/refinement conditions for $DyAl_{0.33(2)}Ga_{2.67(2)}$ and $DyAl_{0.85(2)}Ga_{2.15(2)}$.

Refinement composition	$DyAl_{0.32(2)}Ga_{2.68(2)}$	$DyAl_{0.85(2)}Ga_{2.15(2)}$
Structure type	$Ta(Rh_{0.33}Pd_{0.67})_3$	$BaPb_3$
Space group	$P6_3/mmc$	R-3m
Pearson symbol	$hP40$	$hR36$
Cell par.		
a, Å	6.1649(1)	6.1702(1)
c, Å	23.0792(1)	20.7797(1)
Cell volume (Å^3)	759.63(3)	685.13(3)
Z	10	9
Calculated density (g/cm^3)	7.82	7.32
X-ray machine	Guinier Huber G 670	
Wavelength	$CuK\alpha_1$	
Two-theta range	5.0–100.79	5.0–100.31
Refinement, program	WINCSD	
U, V, W	0.05199; −0.05882; 0.03532	0.13887; −0.10022; 0.05159
R_I	0.0782	0.0970
R_P	0.1106	0.1167
R_{wP}	0.9204	0.7903

$R_I = \sum|I_o - I_c|/\sum|I_o|$, $R_p = \sum|y_{oi} - y_{ci}|/\sum|y_{oi}|$, I_o – obs. intensity; I_c – calc. intensity; y_{oi} – exp. intensity point; y_{ci} – calc. intensity point.

Further substitution causes the next phase transition. According to the X-ray phase analyses, the sample with the nominal composition $Dy_{25}Al_{10}Ga_{65}$ ($DyAl_{0.4}Ga_{2.6}$) does not belong to the $TiNi_3$-, $BaPb_3$- or $AuCu_3$-type. Crystal structure of this phase was successfully refined in $Ta(Rh_{0.33}Pd_{0.67})_3$ type, standardized crystallographic are represented in Tables 1, 3 and 4. Fig. 1b shows the graphical representation of the Rietveld refinement.

By comparison with the literature data we can conclude that the compound $DyAl_{2.6-0.8}Ga_{0.4-2.2}$ can be considered as a metastable pseudo-binary compound stabilized by the Al/Ga substitution, similar to rapid solidification as reported in Ref. [6]. $DyAl_{0.33(2)}Ga_{2.67(2)}$ ($Ta(Rh_{0.33}Pd_{0.67})_3$-type) can be considered as a stabilization of the ht1-$DyGa_3$ phase, at a temperature 50 K higher than the temperature of its existence.

Since the valence electron concentration remains the same during the isoelectronic Al/Ga substitution we suppose that the stabilizations are induced by the changes of the internal lattice

Table 2
Atomic coordinates and isotropic displacements parameters of $DyAl_{0.33(2)}Ga_{2.67(2)}$.

Atom	Site	x/a	y/b	z/c	$B_{iso/eq}$[b], Å^2
Dy1	2b	0	0	1/4	0.97(4)
Dy2	4f	1/3	2/3	0.0430(1)	1.12(4)
Dy3	4f	2/3	1/3	0.3504(1)	1.07(4)
$X1$[a]	6h	0.5186(2)	0.0372(2)	1/4	1.36(7)
$X2$[a]	12k	0.1728(2)	2x	0.1494(1)	1.20(6)
$X3$[a]	12k	0.1433(1)	2x	0.5521(1)	0.95(5)

[a] Mixed occupation. $X1$ = 0.98(1)Ga + 0.02(1)Al; $X2$ = 0.82(1)Ga + 0.18(1)Al; $X3$ = 0.92(1)Ga + 0.08(1)Al.
[b] $B_{iso/eg} = (8\pi^2/3)\sum_i\sum_j\sum_{ij} a_i a_j a_i a_j$.

Table 3
Atomic coordinates and isotropic displacements parameters of $DyAl_{0.85(2)}Ga_{2.15(2)}$.

Atom	Site	x/a	y/b	z/c	$B_{iso/eg}$[b], Å^2
Dy1	3a	0	0	0	1.50(3)
Dy2	6c	0	0	0.2166(1)	1.02(2)
$X1$[a]	9e	1/2	0	0	1.27(4)
$X2$[a]	18h	0.4796(1)	0.5203(1)	0.2237(1)	1.43(3)

[a] Mixed occupation. $X1$ = 0.43(1)Al + 0.57(1)Ga; $X2$ = 0.21(1)Al + 0.79(1)Ga.
[b] $B_{iso/eg} = (8\pi^2/3)\sum_i\sum_j\sum_{ij} a_i a_j a_i a_j$.