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CRYSTAL STRUCTURE OF PHASES FROM $GdNiIn_{1-x}Al_x$ SOLID SOLUTION

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The two phases within a continuous solid solution between the GdNiIn and GdNiAl compounds were synthesized and their crystal structures were determined on the basis of X-ray single crystal data: GdNiAl (ZrNiAl type, P-62m, a = 0.70200(5), c = 0.39148(1) nm, R_1 = 0.0091, wR_2 = 0.0202) and $GdNiIn_{0.48(1)}Al_{0.52(1)}$ (ZrNiAl type, P-62m, a = 0.72500(5), c = 0.38532(1) nm, R_1 = 0.0151, wR_2 = 0.0323). Features of the structure were briefly discussed.

Keywords: Aluminum, Indium, single crystal, crystal structure.

Introduction

Ternary *RE*NiIn and *RE*NiAl compounds with a hexagonal ZrNiAl-type structure are characterized by complex magnetic behaviour over a wide temperature range [1–4]. The relationship between magnetic properties and the electronic structure of intermetallic compounds with ZrNiAl-type structure was analyzed and confirmed by magnetometric, neutron diffraction, and spectroscopic measurements [5]. The GdNiAl compound is characterized by a complex magnetic structure with three transitions (ferromagnetic at 60 K and two antiferromagnetic orderings at 31 and 14 K) [6–8]. Interesting physical properties show the GdNiIn compound [9–11]. The magnetic properties of several $(Gd_{1-x}Er_x)$NiAl alloys were undertaken using magnetic and heat capacity measurements in an attempt to understand the table-like magnetocaloric effect previously observed in $(Gd_{0.54}Er_{0.46})$NiAl [12].

The formation of continuous solid solutions between isostructural *RE*NiIn and *RE*NiAl (*RE* = Ce, Y, Gd, Tb) compounds was observed [13–18]. Here we present the results of the crystal structure determination of some phases of the $GdNiIn_{1-x}Al_x$ solid solution [16] for the single crystals from alloys with two different compositions.

Experimental details

At the first step, ingots of gadolinium (Smart Elements), nickel wire (Chempur), indium tear drops (Smart Elements), and aluminum lumps (Smart Elements), all metals with purities more than 99.9% were melted in arc-furnace under argon atmosphere. Further arc-melted alloys with composition GdNiAl and $GdNiIn_{0.5}Al_{0.5}$ were placed in small tantalum tubes and arc-welded under an argon pressure of about 600 mbar for single crystal growing. The tube was enclosed in an evacuated silica ampoule, and the sample was heated in a Naberterm HTCT 01/16 furnace. At first, samples were heated to 1373 K within 6 h and held at that temperature for 2 h, cooled at a rate of 3 K/h to 1173 K and held at that temperature for 6 h. Finally, the samples were cooled to room temperature within 20 h. Irregularly shaped crystal fragments were selected from the crushed samples and were first investigated with a Buerger precession camera with white molybdenum radiation to check their quality for intensity data collection. Intensity data were collected at room temperature with a STOE IPDS II diffractometer (graphite monochromatized Mo K_α-radiation; oscillation mode, room temperature). The crystal structure was solved and refined with programs from the JANA 2006 [19]. The measured crystals were analyzed semi-quantitatively with a Zeiss EVO MA10 scanning electron microscope. The experimentally determined element ratio for the GdNiAl: 34(2) at.% Gd, 32(2) at.% Ni, 34(2) at.% Al, and for the $GdNiIn_{0.48(1)}Al_{0.52(1)}$: 35(2) at.% Gd, 30(2) at.% Ni, 15(2) at.% In, 20(2) at.% Al.

Results and discussion

GdNiIn and GdNiAl compounds form a continuous solid solution with the ZrNiAl-type structure, described by X-ray powder diffraction [16]. To confirm these results crystal structure of GdNiAl and $GdNiIn_{0.48(1)}Al_{0.52(1)}$ phases were synthesized and refined from single crystal data. Structure refinement (was performed within the ZrNiAl-type structure model) for $GdNiIn_{0.48(1)}Al_{0.52(1)}$ phase showed that 3*g* position is occupied by a mixture of In/Al atoms. An increase in the content of the larger atoms of In in this position leads to a rise of the *a* lattice parameter and a decrease of the *c* parameter: $a = 0.72500(5)$, $c = 0.38532(1)$ nm. For both structures all positions are fully occupied. Details on the crystallographic data and the structure refinements are listed in Table 1. Atomic coordinates and anisotropic displacement parameters in the refined structures are listed in Table 2 and interatomic distances - in Table 3.

Representatives of the ZrNiAl-type structure are built up of two types of layers. The first one contains the Gd atoms located at the Wyckoff positions 3*f* (*x*, 0, 0) and one of the Ni atoms at the 1*a* (0, 0, 0) position (Fig. 1, *a*). The second layer is formed of the *p*-element (Al, In or Al/In) atoms at the positions 3*g* (*x*, 0, 1/2) and Ni atoms located at 2*d* (2/3, 1/3, 1/2) position (Fig. 1, *b*). Increasing of interatomic distances with Al substitution by In is expected. However we observed that one Gd–*M* distance of 0.3126 nm (Fig. 2, *a*) is even shorter than the Gd–Al distance of 0.3131 nm (Fig. 2, *b*). This fact can, to a certain extent, explain the decrease in the parameter *c* of the unit cell in the phases of the $GdNiIn_{1-x}Al_x$ solid solution [16] and solid solutions in other related systems, and also indicates the strengthening of the interaction in Gd–*M* pairs.

The unit-cell parameters of phases within the $GdNiIn_{1-x}Al_x$ solid solution [16] change proportionally to the sizes of In and Al atoms [21], as well as to the unit-cell parameters of ternary compounds GdNiIn and GdNiAl. The same regularity can be observed in the phases of the $GdCuIn_{1-x}Al_x$ solid solution [23] (Table 4).

Table 1

Crystallographic data and structure refinement for GdNiAl and $GdNiIn_{0.48(1)}Al_{0.52(1)}$ ZrNiAl-type structure, space group *P*-62*m*, *Z* =3

Formula	GdNiAl	$GdNiIn_{0.48(1)}Al_{0.52(1)}$
Pearson symbol	*hP*9	
Lattice parameters, nm	a = 0.70200(5) c = 0.39148(1) V = 0.16708(2)	a = 0.72500(5) c = 0.38532(1) V = 0.17540(2)
Radiation; λ, nm	Mo $K\alpha$; 0.071073	
Temperature, K	293	
Density calcd., g/cm^3	7.2431	8.1043
Absorption coeff. nm$^{-1}\cdot10^6$	38.562	40.549
F(000)	315	367
θ range	3.36–35.01	3.24–34.79
hkl range	±11, ±11, -5/6	-9/11, ±11, ±6
No. of reflections	6114	4361
Independent reflections/parameters	305/15	316/16
Reflections with $I > 2\sigma(I)$	298	309
Goodness-of-fit F^2	0.83	1.16
R_1/wR_2 for $I > 2\sigma(I)$	0.0086/0.0201	0.0139/0.0320
R_1/wR_2 for all data	0.0091/0.0202	0.0151/0.0323
Flack parameter	-0.02(2)	0.10(2)
Largest diff. peak/hole, e/nm$\cdot10^3$	0.45/-0.50	0.71/-0.84

Table 2

Atomic coordinates and anisotropic displacement parameters in the GdNiAl and $GdNiIn_{0.48(1)}Al_{0.52(1)}$ structures

Atom	Wyck.	x	y	z	$U_{eq}\cdot10^2$, nm^2
		GdNiAl			
Gd	3*f*	0.41778(3)	0	0	0.0088(1)
Ni1	1*a*	0	0	0	0.0098(2)
Ni2	2*d*	2/3	1/3	1/2	0.0117(2)
Al	3*g*	0.7658(2)	0	1/2	0.0093(3)
Atom		U_{11}	U_{22}	U_{33}	U_{12}
Gd		0.0085(1)	0.0084(1)	0.0095(1)	0.0042(1)
Ni1		0.0105(1)	0.0105(2)	0.0085(4)	0.0052(1)
Ni2		0.0125(1)	0.0125(1)	0.0101(3)	0.0062(1)
Al		0.0087(4)	0.0098(5)	0.0098(4)	0.0049(2)
		$GdNiIn_{0.48(1)}Al_{0.52(1)}$			
Gd	3*f*	0.41510(5)	0	0	0.0122(1)
Ni1	1*a*	0	0	0	0.0207(5)
Ni2	2*d*	2/3	1/3	1/2	0.0146(3)
M	3*g*	0.75464(11)	0	1/2	0.0119(3)
Atom		U_{11}	U_{22}	U_{33}	U_{12}
Gd		0.0130(1)	0.0120(2)	0.0114(1)	0.0060(1)
Ni1		0.0218(6)	0.0218(6)	0.0187(8)	0.0109(3)
Ni2		0.0155(4)	0.0155(4)	0.0126(5)	0.0078(2)
M		0.0108(4)	0.0120(4)	0.0133(4)	0.0060(2)

M = 0.48(1) In + 0.52(1) Al

Table 3

Interatomic distances (δ, nm) and CN of atoms in the GdNiAl and $GdNiIn_{0.48(1)}Al_{0.52(1)}$ structures

Atom		δ, nm	CN	Atom		δ, nm	CN
GdNiAl				$GdNiIn_{0.48}Al_{0.52}$			
Gd	4Ni2	0.28757(1)		Gd	4Ni2	0.29103(1)	
	Ni1	0.29329(3)			Ni1	0.30094(4)	
	2Al	0.3131(1)	15		2*M*	0.31260(7)	15
	4Al	0.32115(9)			4*M*	0.32525(6)	
	4Gd	0.36495(2)			4Gd	0.37786(2)	
Ni1	6Al	0.25561(5)	9	Ni1	6*M*	0.26223(5)	9
	3Gd	0.29328(2)			3Gd	0.30093(3)	
Ni2	3Al	0.27546(4)	9	Ni2	3*M*	0.27907(6)	9
	6Gd	0.28758(1)			6Gd	0.29103(1)	
Al	2Ni1	0.25562(9)		*M**	2Ni1	0.26223(5)	
	2Ni2	0.2755(1)			2Ni2	0.27907(6)	
	2Al	0.2848(2)	12		2*M*	0.3081(1)	12
	2Gd	0.3131(1)			2Gd	0.31258(7)	
	4Gd	0.32115(2)			4Gd	0.32525(2)	

*M = 0.48(1) In + 0.52(1) Al

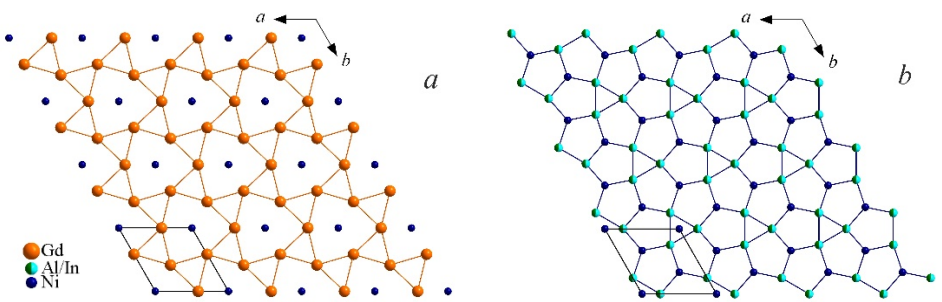

Fig. 1. Type of the layers in the $GdNiIn_{0.48}Al_{0.52}$ structure.

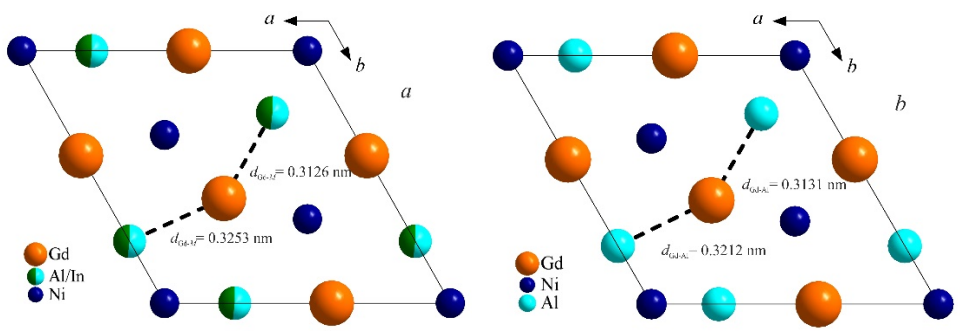

Fig. 2. The unit cell of $GdNiIn_{0.48}Al_{0.52}$ (*a*) and GdNiAl (*b*) along the *ab* projection.

Table 4

Cell parameters of the phases in Gd*T*$In_{1-x}Al_x$ (*T* = Ni, Cu) solid solutions (ZrNiAl-type structure, space group *P*-62*m*)

Phase	*a*, nm	*c*, nm
GdNiIn [b] [9]	0.7452	0.3837
$GdNiIn_{0.5}Al_{0.5}$ [b] [this work]	0.7250	0.3853
$GdNiIn_{0.3}Al_{0.7}$ [a] [16]	0.7153	0.4076
GdNiAl [b] [7]	0.7021	0.3921
[this work]	0.7020	0.3915
GdCuIn [a] [22]	0.7470	0.3993
$GdCuIn_{0.7}Al_{0.3}$ [b] [23]	0.7376	0.3989
$GdCuIn_{0.3}Al_{0.7}$ [a] [16]	0.7145	0.4078
GdCuAl [b] [23]	0.7054	0.4062

[a] Lattice parameters from powder data

[b] Lattice parameters from single crystal data

Conclusions

Single crystals of the GdNiAl and $GdNiIn_{0.48(1)}Al_{0.52(1)}$ phases were synthesized using a special technique, and their crystal structures, which are representatives of the ZrNiAl-type structure, were refined. The replacement of aluminum atoms by indium atoms in the structure $GdNiIn_{0.48(1)}Al_{0.52(1)}$ occurs in position 3*g* (*x* 0 1/2) of space group *P*-62*m*, which is characterized by a change in the coordinates of atoms along the *a* and *b* directions. The unit-cell parameters of phases within the $GdNiIn_{1-x}Al_x$ solid solution change proportionally to the sizes of In and Al atoms, as well as to the unit-cell parameters of the ternary compounds GdNiIn and GdNiAl.

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РЕЗЮМЕ

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КРИСТАЛІЧНА СТРУКТУРА ФАЗ ТВЕРДОГО РОЗЧИНУ $GdNiIn_{1-x}Al_x$

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Неперервний твердий розчин зі структурою типу ZrNiAl, який формується на основі сполук GdNiIn та GdNiAl, раніше досліджений методом рентгенівської порошкової дифракції. Для підтвердження цих результатів синтезовано монокристали фаз GdNiAl і $GdNiIn_{0,48(1)}Al_{0,52(1)}$ та уточнено їхню кристалічну структуру.

Попередньо синтезовані методом електродугового сплавляння зразки складів GdNiAl та $GdNiIn_{0,5}Al_{0,5}$ піддали спеціальній термічній обробці. У результаті одержали монокристали неправильної форми з металевим блиском, які протестували методом Лауе (прецесійна камера Бюргера, Mo K-проміння) та підтвердили гексагональну сингонію для них. Якісний та кількісний склад кристалів підтверджено результатами EDX аналізу (скануючий електронний мікроскоп Zeiss EVO MA10). Розшифрування й уточнення кристалічної структури обох фаз виконано в рамках моделі структурного типу ZrNiAl із використанням пакета програм JANA 2006 на основі масивів експериментальних відбить *hkl,* одержаних на дифрактометрі Stoe IPDS II (Mo *K*α-проміння): GdNiAl (ZrNiAl*, P*-62*m*) – a = 0,70200(5), c = 0,39148(1) нм, R_1 = 0,0091, wR_2 = 0,0202) та $GdNiIn_{0,48(1)}Al_{0,52(1)}$ (ZrNiAl*, P*-62*m*) – a = 0,72500(5), c = 0,38532(1) нм, R_1 = 0,0151, wR_2 = 0,0323.

Атоми статистичної суміші In/Al займають ПСТ 3*g* (x, 0, 1/2) у структурі фази $GdNiIn_{0,48(1)}Al_{0,52(1)}$. Міжатомні віддалі Gd–*M* у структурі цієї фази є коротшими, ніж у тернарній сполуці GdNiAl. Подібні закономірності простежуються у системі $GdCuIn_{1-x}Al_x$.

Ключові слова: алюміній, індій, метод монокристала, кристалічна структура.

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