Structure and Magnetic Properties of $GdPt_2In$ and $GdPt_2Sn$

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Z. Naturforsch. **2009**, *64b,* 170 – 174; received October 29, 2008

The platinum-rich intermetallic compounds $GdPt_2In$ and $GdPt_2Sn$ were synthesized by arc-melting of the elements and subsequent annealing. The structures were refined from single crystal X-ray diffractometer data: $ZrPt_2Al$ type, space group $P6_3/mmc$, a = 455.1(1), c = 899.3(3) pm, $wR2$ = 0.0361, 166 F^2 values, 9 variables for $GdPt_2In$, and a = 453.2(1), c = 906.5(2) pm, $wR2$ = 0.0915, 166 F^2 values, 9 variables for $GdPt_2Sn$. The platinum and indium (tin) atoms build up three-dimensional $[Pt_2In]$ and $[Pt_2Sn]$ networks with short Pt–In (Pt–Sn) distances and Pt_2 dumb-bells (290 and 297 pm in $GdPt_2In$ and $GdPt_2Sn$). The gadolinium atoms have coordination number 14 with 8 Pt and 6 In (Sn) neighbors. Magnetic susceptibility measurements on $GdPt_2In$ show Curie-Weiss behavior with an experimental magnetic moment of 8.06(2) μ_B/Gd atom. $GdPt_2In$ orders ferromagnetically at 27.7(2) K.

Key words: Intermetallics, Gadolinium, Crystal Chemistry

Introduction

Besides the large number of compounds with cubic Heusler-type structure ($MnCu_2Al$ type [1], more than 390 representatives are listed in the Pearson Handbook [2]), only few RET_2X compounds (RE = rare earth metal; T = transition metal; X = element of the 3rd, 4th, or 5th main group) adopt the $ZrPt_2Al$ type [2, 3]. This structure type can be considered as a ternary ordered version of the Na_3As structure [4]. The occurrence of the respective structure type seems to depend on subtle differences in the electronic structures and size requirements. To give an example, in the series of $RE$$Pd_2In$ compounds [5], $LaPd_2In$ [6] and $CePd_2In$ [7] adopt the $ZrPt_2Al$ type while those with the smaller rare earth elements [8] crystallize with the cubic Heusler type. A similar trend is observed for the $RE$$Pt_2In$ series, however, with a different stability range: $ScPt_2In$ [8] is cubic while the compounds $RE$$Pt_2In$ with RE = Y, Gd, Er, Tm, Lu [9, 10] are hexagonal.

Some of the $ZrPt_2Al$ type compounds have interesting magnetic properties. $CePd_2In$ [11] shows a transition to an antiferromagnetically ordered phase at 1.23 K, and $CeCu_2Mg$ [12] is a Kondo lattice system with a huge γ value of 1000 mJ/molK^2. $GdPt_2Sn$ orders ferromagnetically at 20 K [13].

Within our systematic studies [14 – 16, and refs. therein] on structure property relationships of intermetallic gadolinium-based materials, we were also interested in the GdT_2X compounds. Herein we report on the synthesis and single crystal structure refinements of $GdPt_2In$ and $GdPt_2Sn$ and on the magnetic properties of $GdPt_2In$. So far, both compounds had been characterized only on the basis of X-ray powder diffraction.

Experimental Section

Synthesis

Starting materials for the synthesis of the $GdPt_2In$ and $GdPt_2Sn$ samples were ingots of gadolinium (Johnson Matthey), platinum foil (Degussa), and indium and tin granules (Merck), all with stated purities better than 99.9 %. Pieces of the gadolinium ingot were first arc-melted [17] to small buttons under an argon atmosphere. The argon was purified before with molecular sieves, silica gel, and titanium sponge (900 K). For the preparation of $GdPt_2Sn$ a gadolinium button was mixed with pieces of the platinum foil and the tin granules in the ideal 1 : 2 : 1 atomic ratio, and the elements were brought to reaction by arc-melting. The product button was remelted three times to ensure homogeneity. In this way we obtained pure polycrystalline $GdPt_2Sn$.

The preparation of $GdPt_2In$ was slightly different. In a first step we prepared binary $GdPt_2$ by arc-melting. The $GdPt_2$ sample was then ground to a fine powder, mixed with

Table 1. Crystal data and structure refinement for $GdPt_2In$ and $GdPt_2Sn$ (space group $P6_3/mmc$, $Z = 2$).

Compound	$GdPt_2In$	$GdPt_2Sn$
Lattice parameters (Guinier powder data)		
a, pm	455.1(1)	453.2(1)
c, pm	899.3(3)	906.5(2)
Cell volume V, nm^3	0.1613	0.1612
Molar mass, g mol^{-1}	662.25	666.12
Calculated density, g cm^{-3}	13.64	13.72
Absorption coefficient, mm^{-1}	113.5	114.1
$F(000)$, e	538	540
Crystal size, μm^3	$20 \times 40 \times 60$	$10 \times 20 \times 40$
Transm. ratio (max/min)	3.39	1.81
θ range, deg	4–35	4–35
Range in *hkl*	$\pm 7, \pm 7, \pm 14$	$\pm 7, \pm 7, +14$
Total no. reflections	2624	1384
Independent reflections / R_{int}	166 / 0.0725	166 / 0.1461
Reflections with $I \geq 2\sigma(I)$ / R_σ	143 / 0.0230	105 / 0.0595
Data/refined parameters	166 / 9	166 / 9
Goodness-of-fit on F^2	1.176	1.077
Final $R1$ / $wR2$ indices $[I \geq 2\sigma(I)]$	0.0171 / 0.0371	0.0409 / 0.0783
$R1$ / $wR2$ indices (all data)	0.0209 / 0.0361	0.0771 / 0.0915
Extinction coefficient	0.0021(3)	0.0028(7)
Largest diff. peak / hole, e Å^{-3}	1.20 / −1.89	5.92 / −3.24

Table 2. Atomic coordinates and isotropic displacement parameters (pm^2) of $GdPt_2In$ and $GdPt_2Sn$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	Wyck.	x	y	z	U_{eq}
$GdPt_2In$					
Gd	2*c*	1/3	2/3	1/4	78(2)
Pt	4*f*	1/3	2/3	0.58852(4)	85(1)
In	2*a*	0	0	0	92(2)
$GdPt_2Sn$					
Gd	2*c*	1/3	2/3	1/4	66(6)
Pt	4*f*	1/3	2/3	0.5864(2)	63(4)
Sn	2*a*	0	0	0	78(6)

Table 3. Interatomic distances (pm), calculated with the powder lattice parameters of $GdPt_2In$ and $GdPt_2Sn$. All distances within the first coordination spheres are listed. Standard deviations are equal or smaller than 0.1 pm.

$GdPt_2In$				**$GdPt_2Sn$**			
Gd:	6	Pt	300.2	Gd:	6	Pt	300.8
	2	Pt	304.4		2	Pt	304.9
	6	In	345.8		6	Sn	346.1
Pt:	3	In	274.5	Pt:	3	Sn	273.1
	1	Pt	290.4		1	Pt	296.7
	3	Gd	300.2		3	Gd	300.8
	1	Gd	304.4		1	Gd	304.9
	3	Pt	307.2		3	Pt	304.9
In:	6	Pt	274.5	Sn:	6	Pt	273.1
	6	Gd	345.8		6	Gd	346.1

pieces of the indium granules and cold-pressed to a pellet of 6 mm diameter. The pellet was then arc-melted and subsequently remelted three times. The product button was sealed in an evacuated silica ampoule and annealed at 970 K for three weeks in a muffle furnace. For both arc-melting procedures, the total weight loss was smaller than 0.5 %. The silvery polycrystalline $GdPt_2In$ and $GdPt_2Sn$ samples are stable in air over months.

EDX data

Semiquantitative EDX analyses of the two crystals investigated on the diffractometer were carried out by use of a Leica 420i scanning electron microscope with GdF_3, platinum, tin, and InAs as standards. The experimentally observed compositions were close to the ideal values. No impurity elements heavier than sodium (detection limit of the instrument) were found.

X-Ray diffraction

Both powder samples were investigated *via* Guinier patterns (imaging plate detector, Fujifilm BAS–1800 readout system) using Cu$K_{\alpha 1}$ radiation and α-quartz (a = 491.30, c = 540.46 pm) as an internal standard. The hexagonal lattice parameters (Table 1) were obtained from the powder data by least-squares calculations. Proper indexing was ensured through intensity calculations [18]. Our experimental data are in good agreement with the data reported by de Mooij and Buschow for $GdPt_2Sn$ (a = 453.1, c = 906.5 pm) [13] and by Dwight for $GdPt_2In$ (a = 455.1(1), c = 899.7(1) pm) [9].

Single crystals of $GdPt_2In$ and $GdPt_2Sn$ were picked from the crushed samples. Their quality was checked by Laue photographs on a Buerger precession camera (white Mo radiation). Intensity data were collected at r. t. by use of a four-circle diffractometer (CAD4) with graphite-monochromatized MoK_α (λ = 71.073 pm) radiation and a scintillation counter with pulse height discrimination. Scans were taken in the $\omega/2\theta$ mode. Numerical absorption corrections were applied to the data sets. All relevant details concerning the data collections and evaluations are listed in Table 1.

Structure refinements

The isotypy of $GdPt_2In$ and $GdPt_2Sn$ with the hexagonal $ZrPt_2Al$-type structure [3] was clearly obvious from the X-ray powder data. The atomic positions of isotypic $CePd_2In$ [7] were taken as starting parameters, and both structures were refined using SHELXL-97 [19] (full-matrix least-squares on F^2) with anisotropic atomic displacement parameters for all atoms. As a check for deviations from the ideal composition, the occupancy parameters were refined in separate series of least-squares cycles. All sites were fully occupied within three standard deviations. The final difference Fourier syntheses were almost flat (Table 1). The largest residual densities for $GdPt_2Sn$ were close to the platinum sites and most likely resulted from absorption effects. The positional parameters and interatomic distances are listed in Tables 2 and 3.

Further details of the crystal structure investigations may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-420009 ($GdPt_2In$) and CSD-420008 ($GdPt_2Sn$).

Physical property measurements

8.887 mg of the $GdPt_2In$ sample was packed in kapton foil and attached to the sample holder rod of a VSM for measuring the magnetic properties in a Quantum Design Physical-Property-Measurement-System in the temperature range 2.1 – 305 K with magnetic flux densities up to 80 kOe. For heat capacity (C_p) measurements (2.1 – 300 K) 11.162 mg of $GdPt_2In$ was glued to the platform of a precalibrated heat capacity puck using *Apiezon N grease*.

Results and Discussion

Crystal chemistry

$GdPt_2In$ and $GdPt_2Sn$ crystallize with the hexagonal $ZrPt_2Al$-type structure, space group $P6_3/mmc$. Geometrically, this structure is derived from the well known AlB_2 type by an ordered replacement of every other site within the planar hexagons by Pt_2 dumb-bells which extend in the *c* direction (Fig. 1). The tin (indium) atoms take the aluminum and the gadolinium atoms the remaining boron sites. Due to the insertion of the dumb-bells, the structures are built up from three-dimensional $[Pt_2Sn]$ and $[Pt_2In]$ networks.

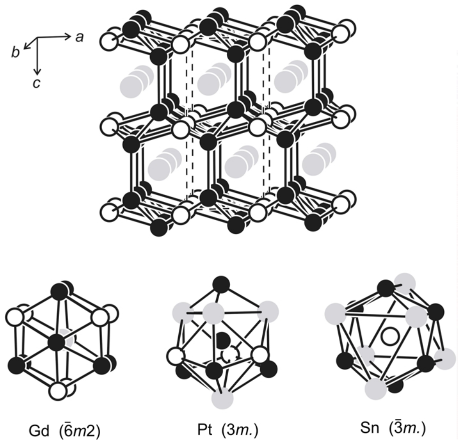

Fig. 1. The crystal structure of $GdPt_2Sn$. Gadolinium, platinum and tin atoms are drawn as medium grey, black filled and open circles, respectively. The three-dimensional $[Pt_2Sn]$ network is emphasized. The near-neighbor coordination is presented at the bottom.

In the following discussion, when we quote interatomic distances, we refer to $GdPt_2Sn$. Within the $[Pt_2Sn]$ network each tin atom has a strongly distorted octahedral platinum coordination with Pt–Sn distances of 273 pm, close to the sum of the covalent radii [20] of 269 pm, indicating substantial Pt–Sn bonding. The Pt–Pt distances within the Pt_2 dumb-bells of 297 pm are slightly longer than in *fcc* platinum (d(Pt–Pt) = 277 pm) [21].

The gadolinium atoms fill larger cages of coordination number 14 (8 Pt + 6 Sn) within the $[Pt_2Sn]$ network (Fig. 1). They bond to the network *via* the Gd–Pt contacts (301 and 305 pm, close to the sum of the covalent radii of 290 pm [20]). The gadolinium atoms in both compounds are well separated from each other. The shortest Gd–Gd distances correspond to the lattice parameters *a* of 455.1(1) and 453.2(1) pm in $GdPt_2In$ and $GdPt_2Sn$, respectively.

Magnetic properties of $GdPt_2In$

The temperature dependence of the reciprocal magnetic susceptibility of $GdPt_2In$ is presented in Fig. 2. Above 50 K we observe Curie-Weiss behavior with an experimental effective magnetic moment of 8.06(2) μ_B/Gd atom, in good agreement with the free ion value of 7.94 μ_B for Gd^{3+}. Extrapolation of the χ^{-1} *vs.* T data to $\chi^{-1} = 0$ led to a Weiss constant

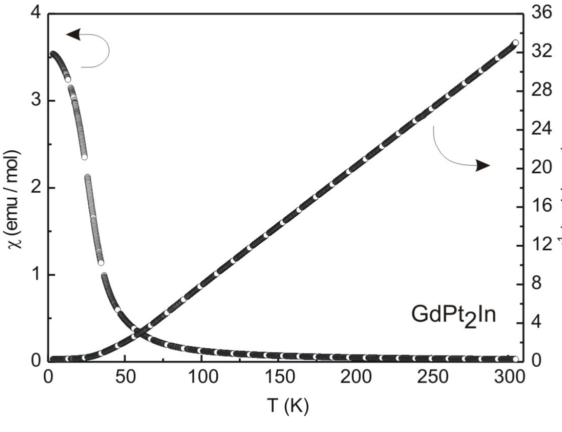

Fig. 2. Temperature dependence of the magnetic susceptibility (χ and χ^{-1} data) of $GdPt_2In$ measured at 10 kOe.

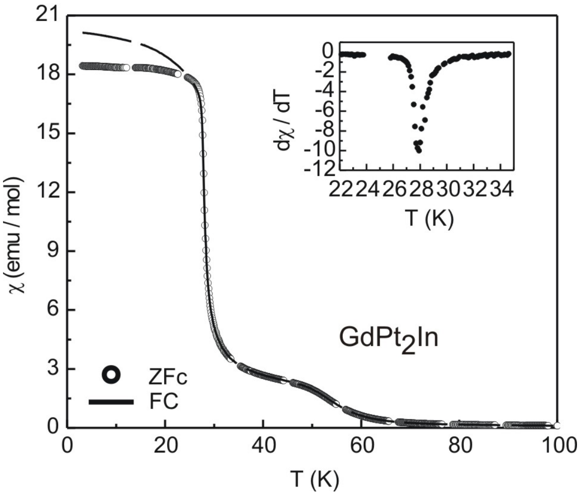

Fig. 3. Low-temperature susceptibility (zero-field-cooling and field-cooling modus) of $GdPt_2In$ at 100 Oe (kink-point measurement). The inset shows the derivative $d\chi/dT$ of the zero-field-cooling curve with a sharp peak at the Curie temperature of T_C = 27.9 K. For details see text.

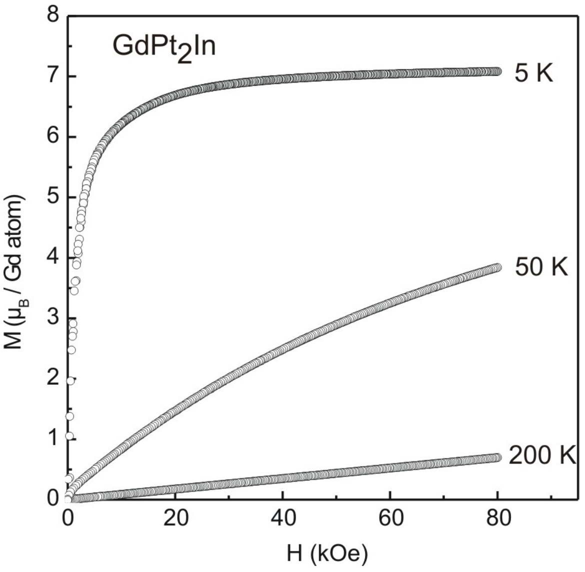

Fig. 4. Magnetization isotherms of $GdPt_2In$ measured at 5, 50 and 200 K.

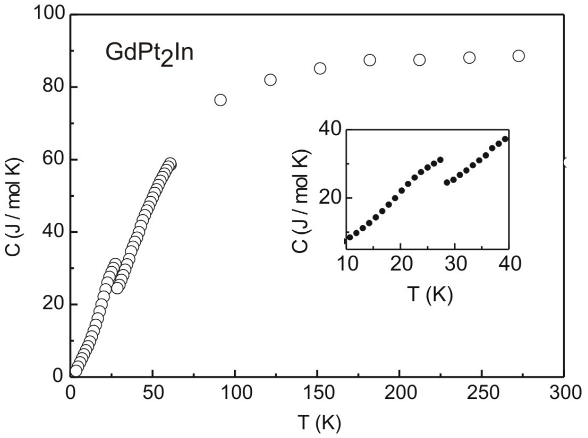

Fig. 5. Temperature dependence of the specific heat of $GdPt_2In$ in zero magnetic field. The low-temperature behavior is shown in the inset.

of 34.7(3) K, indicative of ferromagnetic interactions. At low temperature the susceptibility curve shows an anomaly below 40 K indicating ferromagnetic ordering. The exact Curie temperature was determined from a kink-point measurement (Fig. 3). We have therefore measured the susceptibility in a low external field of 100 Oe in the zero-field-cooling and in the field-cooling mode. The derivative $d\chi/dT$ of the zero field cooling measurement resulted in a Curie temperature of T_C = 27.9(1) K. Between 40 and 60 K (H = 100 Oe) there is another minor anomaly, smaller than the detectability limit of X-ray powder diffraction, that belongs to a trace amount of either GdPt [22] or $GdPt_2$ [23], which order ferromagnetically at T_C = 66 and 37 K, respectively. This anomaly already vanishes at an external field of 500 Oe.

The magnetization isotherms taken at 5, 50 and 200 K are shown in Fig. 4. At 200 K we observe an almost linear increase of the magnetization with the applied field as expected for a paramagnetic material. In contrast, at 5 K the magnetization almost reaches saturation at an external field strength of 0.4 T, and the saturation magnetization (sm) at 80 kOe amounts to $\mu_{\mathrm{exp(sm)}}$ = 7.08(2) μ_B/Gd atom, in good agreement with the theoretical value for Gd^{3+} at 7 μ_B/Gd atom ($g \times J$). Considering the very small hysteresis, $GdPt_2In$ can be classified as a soft ferromagnet. In Fig. 5 the specific heat (C_p) data is plotted for $GdPt_2In$. The Curie temperature of 27.7(2) K is characterized by a λ-like anomaly.

Acknowledgements

This work was financially supported by the Deutsche Forschungsgemeinschaft within the priority program SPP 1166 *Lanthanoidspezifische Funktionalitäten in Molekül und Material.* The Ph. D. thesis of W. H. is supported by the Fonds der Chemischen Industrie.

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