

Transition Metal-Gallium Ordering in HfCoGa₂ and HfNiGa₂

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The gallides HfCoGa₂ and HfNiGa₂ were synthesized by arc-melting of the elements and subsequent annealing in glassy carbon crucibles. Their structures have been reinvestigated by X-ray diffraction on powders and single crystals: *I*4mm, *a* = 1222.4(1), *c* = 812.0(1) pm, *w*R₂ = 0.0766, 1464 *F*² values, 64 variables, BASF = 0.41(2) for HfCoGa₂ and *a* = 1224.0(2), *c* = 809.3(2) pm, *w*R₂ = 0.0609, 1499 *F*² values, 63 variables for HfNiGa₂. In contrast to a previous investigation (Dopov. Akad. Nauk Ukr. RSR, Ser. A, 51 (1988)) we observe a fully ordered arrangement of the transition metal and gallium atoms. The crystal chemistry of these gallides is briefly discussed.

Key words: Hafnium, Gallide, Crystal Structure

Introduction

In recent years we have intensively investigated the chemical bonding and physical properties of the family of *AETIn*₂ (*AE* = alkaline earth metal, *T* = transition metal) compounds [1–4, and ref. therein]. These indides crystallize with the MgCuAl₂ structure [5], a ternary ordered version of the well known Re₃B type [6], or with the CaRhIn₂ type [3]. From a topological point of view and based on chemical bonding considerations, these structures can be described as transition metal filled variants of the binary Zintl phase CaIn₂ [7].

The alkaline earth atoms in *AETIn*₂ can also be substituted by rare earth (*RE*) metal atoms. The series *RENiIn*₂ (*RE* = Eu, Gd, Tb, Dy) [8,9], *RERhIn*₂ (*RE* = La–Gd) [10,11], LaPdIn₂ [12], and CePdIn₂ [13] are isotypic with MgCuAl₂. The *RENiIn*₂ compounds with the light rare earth elements crystallize with the PrNiIn₂ type structure [14,15] which is an intergrowth variant of the MgCuAl₂ type. The different structure is most likely due to the larger size of the early rare earth metal atoms. A different behavior is observed for the nickel and rhodium containing compounds with the heavier rare earth elements. There is a slight deviation from the 1:1:2 composition. These indides crystallize with the tetragonal Ho₁₀Ni₉In₂₀ structure [12,16,17]. With palladium as transition metal component the *REPdIn*₂ compounds [12] with the late rare earth metals adopt the tetragonal HfNiGa₂ type [18]. The ordering of the nickel and gallium positions in

that structure type, however, has not been reported. We have recently refined the TmPdIn₂ structure [12] which showed full palladium-indium ordering. In order to compare this structure with the prototype, we reinvestigated the structures of HfNiGa₂ and HfCoGa₂. The results are reported herein.

Experimental Section

Synthesis

Starting materials for the preparation of HfCoGa₂ and HfNiGa₂ were hafnium chips (Heraeus), cobalt powder (Merck, 1 μm), nickel powder (Johnson Matthey, 1 μm), and gallium rods (VAW), all with stated purities better than 99.9%. The gallium rods were crushed to small pieces at liquid nitrogen temperature. The three components were subsequently mixed in the ideal 1:1:2 composition and cold-pressed to pellets of 6 mm diameter. The total weight of the samples was around 800 mg. The pellets were then arc-melted [19] under an argon atmosphere of ca. 600 mbar. The argon was purified over molecular sieves, silica gel and titanium sponge (900 K). The resulting buttons were turned around in the water-cooled crucible and melted again in order to achieve homogeneity. The total weight losses after the melting procedures were smaller than 0.5 weight-%. The HfNiGa₂ sample was subsequently placed in a glassy carbon crucible (SIGRADUR® G, glassy carbon, type GAZ006) and annealed at ca. 1300 K for 2 h in a water-cooled sample chamber [20] in a high-frequency furnace (Hüttinger Elektronik, Freiburg, Typ TIG 1.5/300). The HfCoGa₂ button was also placed in a glassy carbon crucible but further sealed in

Empirical formula	HfCoGa ₂	HfNiGa ₂
Formula weight	376.86	376.64
Unit cell dimensions	$a = 1222.4(1)$ pm	$a = 1224.0(2)$ pm
(Guinier powder data)	$c = 812.0(1)$ pm	$c = 809.3(2)$ pm
	$V = 1213.3$ nm ³	$V = 1212.5$ nm ³
Calculated density	10.32 g/cm ³	10.32 g/cm ³
Crystal size	50 × 50 × 100 μm ³	20 × 20 × 60 μm ³
Transmission ratio (max/min)	1.32	1.32
Absorption coefficient	70.9 mm ⁻¹	71.9 mm ⁻¹
$F(000)$	3220	3240
θ Range for data collection	3° to 35°	2° to 35°
Range in hkl	$-19 < h < 17; \pm 19; -12 < l < 13$	$\pm 19; \pm 19; \pm 13$
Total no. of reflections	8763	5800
Independent reflections	1464 ($R_{\text{int}} = 0.0755$)	1499 ($R_{\text{int}} = 0.0831$)
Reflections with $I > 2\sigma(I)$	1439 ($R_{\text{sigma}} = 0.0340$)	1262 ($R_{\text{sigma}} = 0.0593$)
Data / parameters	1464 / 64	1499 / 63
Goodness-of-fit on F^2	1.132	1.026
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0298$	$R1 = 0.0365$
	$wR2 = 0.0761$	$wR2 = 0.0574$
R Indices (all data)	$R1 = 0.0305$	$R1 = 0.0518$
	$wR2 = 0.0766$	$wR2 = 0.0609$
Extinction coefficient	0.00071(6)	0.00056(2)
Flack parameter	—	-0.02(3)
BASF	0.41(2)	—
Largest diff. peak and hole	2.61 and -5.19 e/Å ³	2.55 and -3.56 e/Å ³

Table 1. Crystal data and structure refinement of HfCoGa₂ and HfNiGa₂ (space group $I4mm$, $Z = 20$).Table 2. Atomic coordinates and equivalent isotropic displacement parameters (pm²) of HfCoGa₂ and HfNiGa₂ (space group $I4mm$).

Atom	Wyckoff position	x	y	z	U_{eq}
HfCoGa₂					
Hf1	8d	0.28392(4)	0	0.12608(6)	63(1)
Hf2	8c	0.29907(3)	x	0.13546(6)	62(1)
Hf3	2a	0	0	0.0540(1)	76(2)
Hf4	2a	0	0	0.5200(1)	118(2)
Co1	8d	0.2151(2)	0	0.4860(2)	101(3)
Co2	8c	0.3378(1)	x	0.4818(2)	54(3)
Co3	4b	0	1/2	0.4005(3)	85(4)
Ga1	16e	0.35153(8)	0.85892(8)	0.3870(1)	72(2)
Ga2	8d	0.1637(1)	0	0.7986(2)	72(2)
Ga3	8d	0.3824(1)	0	0.6501(2)	85(2)
Ga4	8c	0.36848(8)	x	0.7894(2)	72(2)
HfNiGa₂					
Hf1	8d	0.28711(5)	0	0.1272(1)	74(1)
Hf2	8c	0.29617(3)	x	0.1358(1)	76(1)
Hf3	2a	0	0	0.0626(2)	79(3)
Hf4	2a	0	0	0.5125(2)	86(3)
Ni1	8d	0.2154(2)	0	0.4847(3)	76(4)
Ni2	8c	0.3384(1)	x	0.4747(3)	65(4)
Ni3	4b	0	1/2	0.4001(5)	102(7)
Ga1	16e	0.3519(1)	0.8585(1)	0.3842(3)	78(2)
Ga2	8d	0.1609(2)	0	0.7954(3)	83(3)
Ga3	8d	0.3825(2)	0	0.6483(3)	101(4)
Ga4	8c	0.3671(1)	x	0.7884(3)	78(4)

a silica ampoule and annealed at 1270 K for 7 d in a muffle furnace. Both gallides were obtained in pure form after the annealing procedures. No reaction with glassy carbon was

observed. The samples are light gray and stable in moist air. Single crystals exhibit metallic luster.

X-ray investigations

Both samples were characterized through Guinier powder patterns using Cu-K α_1 radiation and α -quartz ($a = 491.30$ pm, $c = 540.46$ pm) as an internal standard. The lattice parameters (Table 1) were obtained from least-squares fits of the powder data. To ensure correct indexing, the patterns were compared with calculated ones [21] taking the atomic positions from the structure refinements. The lattice parameters determined from the powders and the single crystals agreed well. Reasonable agreement is also observed with the lattice parameters determined by Markiv *et al.* [18]: $a = 1223.7(3)$, $c = 808.3(1)$ pm for HfNiGa₂ and $a = 1219.2$, $c = 814.2$ for HfCoGa₂.

Irregularly shaped silvery single crystals of HfNiGa₂ and HfCoGa₂ were selected from the annealed, crushed samples. They were examined by Laue photographs on a Buerger precession camera (Mo radiation) equipped with an image plate system (Fujifilm BAS-1800) in order to establish suitability for intensity data collection. Single crystal intensity data of the HfNiGa₂ crystal have been collected on a four-circle diffractometer (CAD4) with graphite monochromatized Mo-K α radiation (71.073 pm) and a scintillation counter with pulse height discrimination. The scans were performed in the $\omega/2\theta$ mode. An empirical absorption correction was applied on the basis of Ψ -scan data. The HfCoGa₂ crystal was measured on an IPDS-II diffractome-

Hf1:	2T2	274.2 / 279.2	T1:	1Ga3	244.1 / 243.6	Ga2:	2T2	248.0 / 245.4	Table 3. Interatomic distances in the gallides HfTGa ₂ (T = Co/Ni) calculated with the powder lattice parameters. Standard deviations are all equal or less than 0.5 pm.
	2Ga4	279.5 / 281.3		2Ga4	248.5 / 248.8		1T1	261.5 / 260.2	
	2Ga1	281.1 / 281.4		2Ga1	253.0 / 254.1		2Hf2	282.7 / 285.8	
	2Ga1	285.4 / 282.1		1Ga2	261.5 / 260.2		2Ga2	283.0 / 278.5	
	2Ga3	301.4 / 298.2		1Hf4	264.4 / 264.6		1Hf3	288.2 / 292.5	
	1Ga2	303.8 / 309.8		2Hf2	274.5 / 278.2		1Ga3	293.2 / 296.2	
	1T1	304.1 / 302.3		1Hf1	304.1 / 302.3		1Hf4	302.0 / 302.0	
	1T3	321.4 / 318.9	T2:	2Ga2	248.0 / 245.4		1Hf1	303.8 / 309.8	
	1T3	345.6 / 341.6		2Ga1	253.0 / 252.4	Ga3:	1T1	244.1 / 243.6	
	1Hf3	352.0 / 355.3		1Ga4	255.4 / 258.7		1T3	248.5 / 247.1	
	2Hf2	366.1 / 362.8		1Hf2	267.4 / 266.9		1T3	249.0 / 249.5	
Hf2:	1T2	267.4 / 266.9		2Hf1	274.2 / 279.2		2Ga1	266.0 / 264.9	
	2T1	274.5 / 278.2		1Hf2	289.1 / 283.8		2Ga1	277.2 / 277.7	
	2Ga2	282.7 / 285.8		1Hf3	286.5 / 288.7		1Ga3	287.5 / 287.7	
	2Ga1	282.8 / 283.1	T3:	2Ga3	248.5 / 247.1		1Ga2	293.2 / 296.2	
	2Ga1	288.3 / 284.4		2Ga3	249.0 / 249.5		2Hf1	301.4 / 298.2	
	1T2	289.1 / 283.8		4Ga1	250.6 / 251.0		2Hf2	331.2 / 331.9	
	1Ga4	305.5 / 306.8		2Hf1	321.4 / 318.9	Ga4:	2T1	248.5 / 248.8	
	1Ga4	315.5 / 308.4		2Hf1	345.6 / 341.6		1T2	255.4 / 258.7	
	2Ga3	331.2 / 331.9	Ga1:	1T3	250.6 / 251.0		2Hf1	279.5 / 281.3	
	2Hf1	366.1 / 362.8		1T2	253.0 / 252.4		2Ga1	280.6 / 279.3	
	1Hf4	359.8 / 366.7		1T1	253.0 / 254.1		1Hf4	294.5 / 293.0	
Hf3:	4T2	286.6 / 288.7		1Ga3	266.0 / 264.9		1Hf3	297.1 / 293.8	
	4Ga2	288.2 / 292.5		1Ga3	277.2 / 277.7		1Hf2	305.5 / 306.8	
	4Ga4	297.1 / 293.8		1Ga4	280.6 / 279.3		1Hf2	315.5 / 308.4	
	4Hf1	352.0 / 355.3		1Hf1	281.1 / 281.4				
	1Hf4	378.4 / 364.1		1Hf2	282.8 / 283.1				
Hf4:	4T1	264.4 / 264.6		1Hf1	285.4 / 282.0				
	4Ga4	294.5 / 293.0		1Hf2	288.3 / 284.4				
	4Ga2	302.0 / 302.0							
	4Hf2	359.8 / 366.7							
	1Hf3	378.4 / 364.1							

ter: 60 mm crystal-detector distance, 0–180° omega range, $\Delta\omega = 1^\circ$, 35 min exposure time per image, integration parameters A = 12.7, B = 4.7, and EMS = 0.041. All relevant crystallographic data and experimental details for both data collections are listed in Table 1.

Structure refinements

An analysis of the data sets revealed only the systematic extinctions for a body-centered lattice leading to the possible space groups $I4/mmm$, $I4mm$, $I\bar{4}2m$, $I\bar{4}m2$, and $I422$ of which space group $I4mm$ was found to be correct during the structure refinements. The atomic positions of TmPdIn₂ [12] were taken as starting parameters and both structures were refined using SHELXL-97 (full-matrix least-squares on F_o^2) [22] with anisotropic atomic displacement parameters for all atoms. In a separate series of least-squares cycles we refined the occupancy parameters of the cobalt(nickel) and gallium positions to check for deviations from the ideal composition, especially since cobalt(nickel) and gallium differ only by three and four electrons, respectively. The following ranges were observed: 99(1)% – 101(1)% and 100(1)% – 104(1)% for the Co and Ga positions in HfCoGa₂; 99(1)% – 103(1)% and 98(1)% – 102(1)% for the Ni and Ga posi-

tions in HfNiGa₂. Since all sites were fully occupied within four (HfCoGa₂) and three (HfNiGa₂) standard deviations the ideal occupancies were assumed again in the final cycles. Refinement of the Flack parameter [23, 24] indicated the correct absolute structure for HfNiGa₂ but twinning by inversion for HfCoGa₂. In the final refinement for the cobalt compound the inversion twin matrix was included. Final difference Fourier syntheses revealed no significant residual peaks (Table 1). The positional parameters and interatomic distances are listed in Tables 2 and 3. Listings of the observed and calculated structure factors are available.*

Discussion

The crystal structures of HfCoGa₂ and HfNiGa₂ have been reinvestigated on the basis of X-ray single crystal diffractometer data. This reinvestigation was stimulated by the recent discovery of the ternary indide TmPdIn₂ which adopts the same structure type. In the

*Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No's. CSD-412752 (HfCoGa₂) and CSD-412753 (HfNiGa₂).

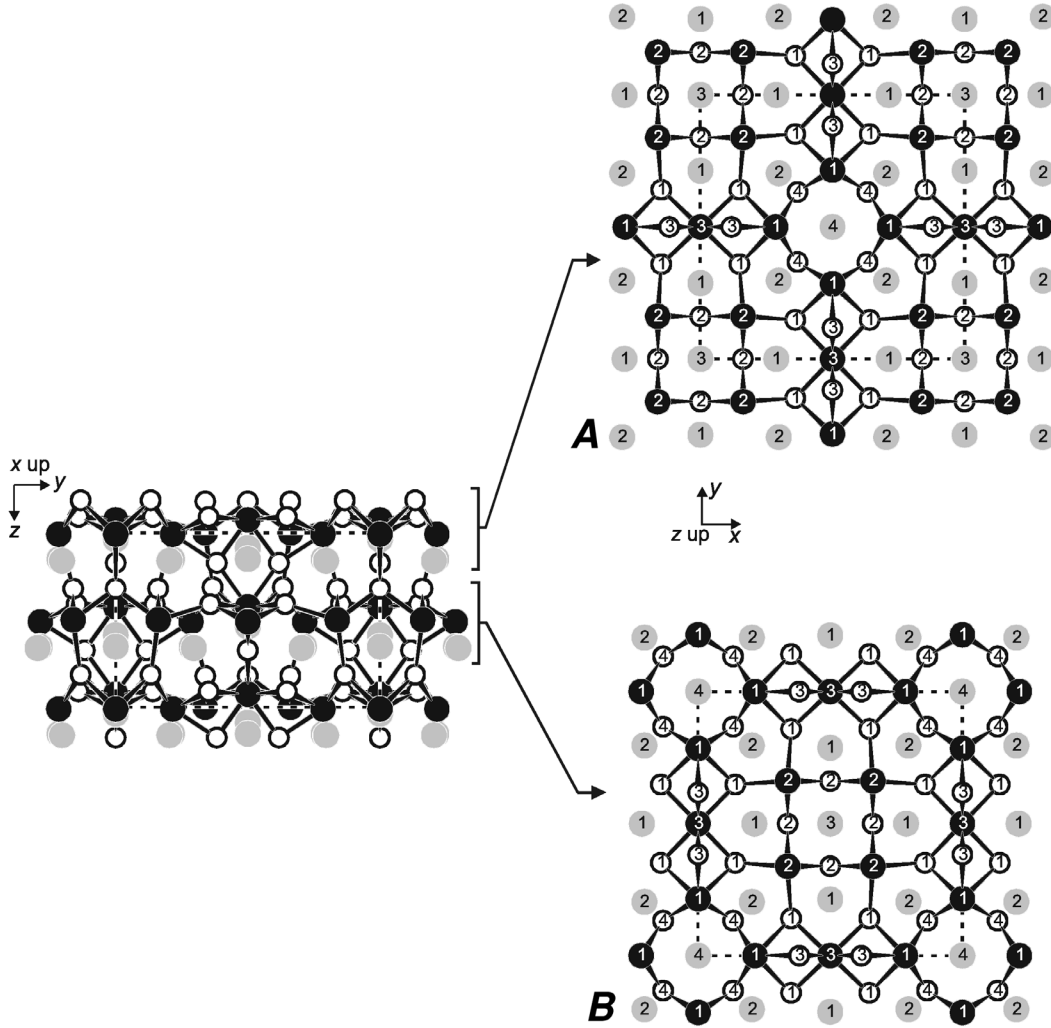


Fig. 1. The crystal structure of HfNiGa₂. At the left-hand side a view along the *x* axis is presented. The relatively complex crystal structure contains the layers *A* (around *z* = 0) and *B* (around *z* = 1/2). The layers *A* and *B* have the same composition; they are shifted by 1/2 1/2 1/2 (body-centered unit cell). Hafnium, nickel, and gallium atoms are drawn as gray, filled, and open circles, respectively. The [NiGa₂] network is emphasized.

previous investigation [18], all Ni/Ga sites have been refined with the same mixed occupancy of 40% Ni and 60% Ga. Since the sample of Markiv *et al.* had the starting composition 0.25 Hf:0.30 Ni:0.45 Ga [18], a mixed occupancy could have been expected. As already mentioned by these authors, a homogeneity range HfNi_{1+x}Ga_{2-x} exists.

The result of the present structure refinements is the unambiguous site assignment for the cobalt(nickel) and gallium atoms which is the same as in TmPdIn₂ [12]. Refinement of the occupancy parameters of the cobalt(nickel) and gallium positions showed essen-

tially full occupancy. Thus, the compositions of the investigated single crystals are close to the ideal ones. Although we collected intensities up to $2\theta = 70^\circ$ and the data / parameters ratio is > 22 , the standard deviations of the occupancy parameters are relatively high. This is certainly due to the small difference in scattering power between cobalt(nickel) and gallium atoms (the ratios of the atomic numbers are 27 : 31 and 28 : 31).

The crystal chemistry of HfNiGa₂ has already been presented by Markiv *et al.* [18]. Here we discuss the HfCoGa₂ and HfNiGa₂ structure briefly with respect to

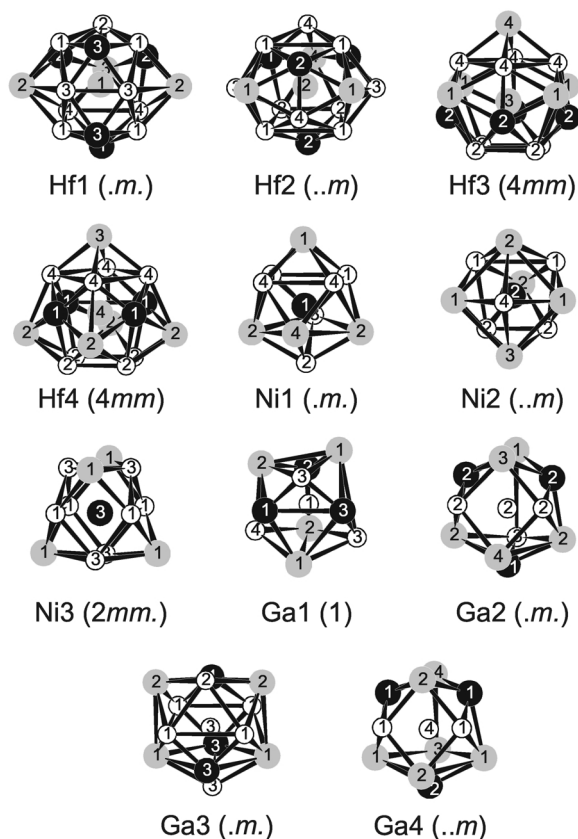


Fig. 2. Coordination polyhedra in the HfNiGa₂ structure. All neighbors listed in Table 3 are shown. Single-digit numbers correspond to the atom designations. The site symmetries are indicated in parentheses.

the cobalt(nickel) / gallium ordering. Due to the large unit cell and the non-centrosymmetry, the HfNiGa₂ structure is somewhat complex to present. In Fig. 1 we present a view along the *x* axis. The structure is composed of two layers *A* (around *z* = 0) and *B* (around *z* = 1/2) of the same composition. Due to the body-centering the *B* layer is formed by shifting the *A* layer by 1/2 1/2 1/2. These layers are connected *via* Ni—Ga and Ga—Ga bonds.

The nickel atoms have between five and eight gallium neighbors at Ni—Ga distances ranging from 244

to 260 pm, slightly larger than the sum of the covalent radii [25]. We can thus assume a significant degree of Ni—Ga bonding. The various Ni—Ga contacts are drawn in Figure 1. The short Ni—Ga and Pd—In distances in HfNiGa₂ and TmPdIn₂ [12] were also a good criterion for the sites assignments during the refinement procedures.

The gallium atoms have between three and six nearest gallium neighbors. The Ga—Ga distances range from 265 to 296 pm. For comparison we look at the structure of elemental gallium [26] where each gallium atom has seven neighbors: one at 248 pm, two at 270, two at 274, and two at 279 pm. The short distance at 248 pm may be considered as a single (two-electron) bond distance, the longer ones as interactions of lower bond order. This is also the case for the various Ga—Ga interactions in HfNiGa₂. Some gallium atoms have additional gallium neighbors at distances longer than 300 pm, *i.e.* 311 pm (Ga1—Ga2) and 325 pm (Ga4—Ga4). These longer contacts should not be considered as bonding.

The coordination polyhedra are presented in Figure 2. The HfNiGa₂ structure has four crystallographically independent hafnium sites. The hafnium atoms have the highest coordination number, CN 17, as expected from the atomic radius. The Hf—Hf distances range from 355 to 367 pm, much larger than in *hcp* hafnium (316 pm average Hf—Hf distance). Also the Hf—Ga distances (281–332 pm) are longer than the sum of the covalent radii (269 pm). Consequently the Hf—Hf and Hf—Ga contacts may be considered as weak. The shorter Hf—Ni distances (265–284 pm) are close to the sum of the covalent radii (262 pm).

Considering the interatomic distances, we can describe the HfNiGa₂ structure by a three-dimensional [NiGa₂] network in which the hafnium atoms fill larger voids. The bonding of the hafnium atoms to this network is based mainly on the Hf—Ni contacts.

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