



Synthesis and crystal structures of the new metal-rich ternary borides Ni₁₂AlB₈, Ni₁₂GaB₈ and Ni_{10.6}Ga_{0.4}B₆—examples for the first B₅ zig-zag chain fragment

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ARTICLE INFO

Article history:

Received 1 March 2010

Received in revised form

30 April 2010

Accepted 9 May 2010

Available online 4 June 2010

Keywords:

Synthesis

Single crystal growth

Structure refinement

EDXS

XRD

Nickel borides

B₅ units

ABSTRACT

Single crystals of the new borides Ni₁₂AlB₈ and Ni_{10.6}Ga_{0.4}B₆ were synthesized from the elements and characterized by XRD and EDXS measurements. The crystal structures were refined on the basis of single crystal data. Ni₁₂AlB₈ (*oC252*, *Cmce*, *a* = 10.527(2), *b* = 14.527(2), *c* = 14.554(2) Å, *Z* = 12, 1350 reflections, 127 parameters, *R*₁(*F*) = 0.0284, *wR*₂(*F*²) = 0.0590) represents a new structure type with isolated B atoms and B₅ fragments of a B–B zig-zag chain. Because the pseudotetragonal metric crystals are usually twinned. Ni_{10.6}Ga_{0.4}B₆ (*oP68*, *Pnma*, *a* = 12.305(2), *b* = 2.9488(6), *c* = 16.914(3) Å, *Z* = 4, 1386 reflections, 86 parameters, *R*₁(*F*) = 0.0394, *wR*₂(*F*²) = 0.104) is closely related to binary Ni borides. The structure contains B–B zig-zag chains and isolated B atoms. Ni₁₂GaB₈ is isotypical to the Al-compound (*a* = 10.569(4), *b* = 14.527(4) and *c* = 14.557(5) Å).

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1. Introduction

Metal-rich borides of “late” (i.e. group 8) 3d-transition metals are important with respect to hardening processes [1]. Furthermore they are promising ceramic materials [2] and show interesting magnetic properties [3]. Their crystal structures are usually dominated by trigonal prisms BM₆. The tendency to form boron–boron bonds is well-known. Diverse oligomeric units follow from the connection of the trigonal prisms via common rectangular sides. In monoborides MB this connection results in the formation of boron–boron zig-zag chains. The different structures of monoborides (FeB-type, CrB-type [4]) originate from different orientation of the chains. For lower B-contents there is a continuous transition from the infinite chains to isolated boron atoms (i.e. Cr₂B: AlCu₂-type and Fe₃B: cementite-type [4]). According to the ratio M:B different boron-subunits are observed. Dimers are observed in W₂CoB₂ [5], B₃-units in W₃CoB₃ [6] and B₄-units in Mo₂IrB₂ [7] usually in trans-orientation. Recently we have reported on the first B₄ unit with a cis-arrangement in

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β-Cr₂IrB₂ [8]. Combinations of different units are known, too, for example in Ru₁₁B₈ [9], o-Ni₄B₃ [10], Cr₅B₃ [11] and Ca₂Os₃B₅ [12].

It is obvious that less or more expanded B–B subunits are observed for M:B ratios between 1 and 2, i.e. MB and M₂B. For the so-called τ-borides, i.e. transition metal borides of a composition (MM')₂₃B₆ [4], isolated B-atoms with square-antiprismatic coordinations are found. Therefore we were motivated by a communication of Stadelmaier et al. [13] on a boron-rich τ-boride Ni₂₀Al₃B₆/Ni₂₀Al₃B₁₂ to study the nature of the enlarged boron content in detail. It was shown on the basis of single crystal data that the reason is the surprising substitution of Al by B₄ tetrahedra: Ni₂₀Al(Al)₂B₆/Ni₂₀Al(B₄)₂B₆ [14]. In continuation we (re)investigated ternary nickel-rich borides with Zn or main group metals (Al, Ga, In and Sn). The focus was on the formation conditions of the different borides, their stability and the growth of single crystals.

The existence of τ-borides is well-known for the systems Ni/Al/B and Ni/Ga/B (Ni/Al/B: [15–17]; Ni/Ga/B: [18,19]). Further ternary compounds were described (i.e. Ni₈AlB₁₁, Ni₅AlB₄ [16], Ni₆GaB₃ [18], Ni₈GaB₁₁ and Ni₁₂GaB₇ [19]), but no details were given.

In this contribution we present some of the results obtained in the course of these investigations, i.e. synthesis and crystal structures of the new ternary borides Ni₁₂AlB₈, Ni₁₂GaB₈ and

$\text{Ni}_{10.6}\text{Ga}_{0.4}\text{B}_6$. In a separate contribution we will report on the Ni containing τ -borides [20–22].

2. Synthesis

2.1. $\text{Ni}_{12}\text{AlB}_8$

$\text{Ni}_{12}\text{AlB}_8$ has been synthesized from nickel (ALFA Aesar, powder, 99.9%), aluminium (ALFA Aesar, powder, 99.8%) and boron (ABCR, powder, 99.5%) in the atomic ratio 12:1.5:8.4. The pelletized powders were put into a corundum crucible, melted in a stream of argon at 1250 °C for 6 h, cooled with 100 °C/h to 600 °C and with 300 °C/h to room temperature. Then the sample was annealed at 950 °C for 100 h. The obtained samples showed no by-products in the X-ray powder pattern (Fig. 1). The powder diagram was completely indexed with a C-centred orthorhombic unit cell indicating a single phase product. The refined lattice parameters were $a=10.521(3)$, $b=14.508(6)$ and $c=14.552(7)$ Å. Increasing the amount of aluminium in the sample the phase NiAl (cP2, $Pm\bar{3}m$) was observed as by-product in the X-ray powder pattern, while decreasing the aluminium content in the sample lead to the occurrence of the binary boride $m\text{-Ni}_4\text{B}_3$ ($mC28$, $C2/c$). Samples with a slightly reduced amount of boron yielded a boron-rich τ -boride ($\text{Ni}_{20}\text{Al}_{3-x}\text{B}_{6+4x}$, $x=1.5\text{--}2$ [14]). Solidification of samples from the melt without annealing yielded nearly pure boron-rich τ -boride as already stated by Stadelmaier et al. [15] (Fig. 1). Transformation to $\text{Ni}_{12}\text{AlB}_8$ and a small amount of NiAl took place during the annealing step between 900 and 950 °C.

The starting compositions for $\text{Ni}_{12}\text{AlB}_8$ and a boron-rich τ -boride (i.e. $\text{Ni}_{20}\text{Al}_{3-x}\text{B}_{6+4x}$, $x=1.5\text{--}2$) are nearly the same. At higher temperatures and without annealing between 900 and 950 °C the τ -boride is the preferred product. We observed the

formation of further phases below 850 °C, which were not yet characterised.

2.2. $\text{Ni}_{12}\text{GaB}_8$

$\text{Ni}_{12}\text{GaB}_8$ has been synthesized from nickel, gallium (ABCR, drops, 99.9%) and boron in the atomic ratio 20:3:12 (=12:1.8:7.2). The pelletized powders were melted in a stream of argon at 1400 °C for 6 h, cooled with 20 °C/h to 1000 and with 300 °C to room temperature. Subsequent annealing was carried out at 900 °C for 48 h. The X-ray diffraction pattern showed NiGa (cP2, $Pm\bar{3}m$) as second phase in the obtained samples. The refined lattice parameters of the C-centred orthorhombic unit cell were $a=10.569(4)$, $b=14.527(4)$ and $c=14.557(5)$ Å. An equally treated pellet with the elements in stoichiometric ratio (12:1:8) gave a powder pattern with $\text{Ni}_{12}\text{GaB}_8$ as the main phase and monoclinic Ni_4B_3 and a boron-rich τ -phase (Ni/Ga/B, $Fm\bar{3}m$) as by-products.

2.3. $\text{Ni}_{10.6}\text{Ga}_{0.4}\text{B}_6$

$\text{Ni}_{10.6}\text{Ga}_{0.4}\text{B}_6$ was obtained from the elements. The original goal was the synthesis of a boron-rich τ -boride. Ni, Ga and B were mixed in a molar ration 20:3:12, pressed into a pellet (total mass: 500 mg), put into a corundum crucible and heated up to 1450 °C under an argon atmosphere. This temperature was maintained for 1 h and then reduced to 1000 °C with a rate of 20 °C/h. Finally the furnace was turned off. The solidified melt was crushed. The XRD pattern showed the lines of $\text{Ni}_{10.6}\text{Ga}_{0.4}\text{B}_6$, NiGa and $o\text{-Ni}_4\text{B}_3$. The refined lattice parameters of $\text{Ni}_{10.6}\text{Ga}_{0.4}\text{B}_6$ were $a=12.243(2)$, $b=2.9583(7)$ and $c=16.975(4)$ Å. The small differences to the values of the single crystal may be caused by the partial Ni/Ga occupation of one site. The intensities of the reflections which were assigned to $\text{Ni}_{10.6}\text{Ga}_{0.4}\text{B}_6$ were in a very good agreement to the theoretical intensities calculated from the single crystal data (see below). It should be mentioned that $\text{Ni}_{10.6}\text{Ga}_{0.4}\text{B}_6$ was obtained only in a few cases. Usual products are $\text{Ni}_{12}\text{GaB}_8$ and/or the corresponding boron-rich τ -boride (see above) with (sometimes) binary alloys Ni/Ga and/or binary Ni borides as by-products.

3. Characterisation

3.1. EDXS: $\text{Ni}_{10.6}\text{Ga}_{0.4}\text{B}_6$

According to the observations in the course of the refinement (electron density) and the structural features (no boron contacts of “Ni11”) the crystal’s composition was checked by EDXS. It turned out that the crystal contains about 4 at% gallium and its composition should be described as $\text{Ni}_{10.6}\text{Ga}_{0.4}\text{B}_6$. This is in good agreement to the XRD results.

EDXS measurements were done with a DSM 960 electron microscope (Fa. Carl Zeiss) equipped with an EDXS tool (Link Analytical Microprobe LEO 1525) at the Institut für Kristallographie (University of Freiburg).

3.2. Powder XRD

XRD patterns were recorded with a STOE Stadi P ($\text{CuK}\alpha$ -1 radiation, Ge-monochromator, image plate detector, Debye-Scherrer geometry and transmission).

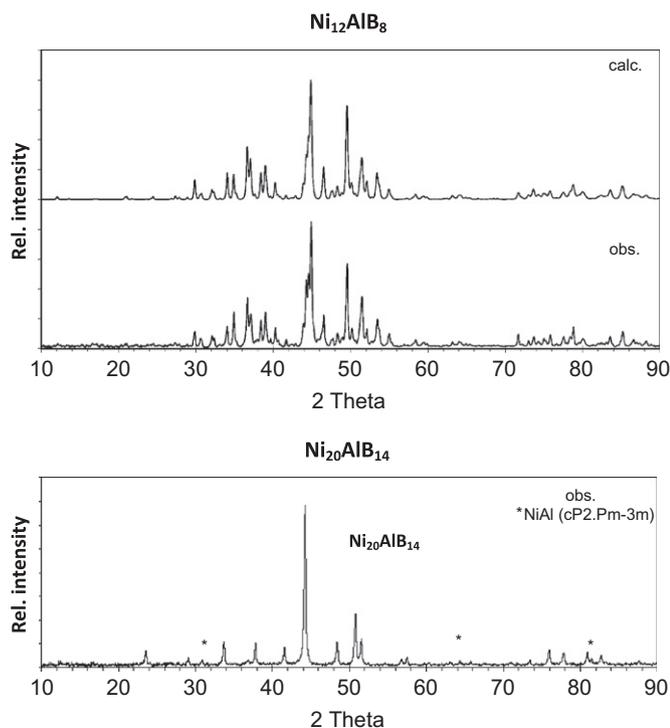


Fig. 1. X-ray diffraction patterns of $\text{Ni}_{12}\text{AlB}_8$ and the τ -boride $\text{Ni}_{20}\text{AlB}_{14}$ (cubic, $a=10.611(1)$ Å).

Table 1
Structure determination and refinement of $Ni_{12}AlB_8$ and $Ni_{10.6}Ga_{0.4}B_6$.

	$Ni_{12}AlB_8$	$Ni_{10.6}Ga_{0.4}B_6$
Crystal shape	irregular fragment	irregular fragment
Crystal colour	black lmetallic ustrous	black-metallic lustrous
Crystal size	$0.1 \times 0.07 \times 0.05 \text{ mm}^3$	$0.1 \times 0.08 \times 0.07 \text{ mm}^3$
Formula weight	817.98 g/mol	715.08 g/mol
Crystal system	orthorhombic	orthorhombic
Space group	<i>Cmce</i> – no. 64	<i>Pnma</i> – no. 62
Lattice constants	$a = 10.527(2) \text{ \AA}$; $b = 14.527(2) \text{ \AA}$; $c = 14.554(2) \text{ \AA}$	$a = 12.305(2) \text{ \AA}$; $b = 2.9488(6) \text{ \AA}$; $c = 16.914(3) \text{ \AA}$
Cell volume	2225.6 \AA^3	613.6 \AA^3
Formula units	12	4
Density, calculated	7.32 g/cm^3	7.74 g/cm^3
Radiation	MoK α , graphite monochromator	MoK α , graphite monochromator
θ -range	$-13 \leq h \leq 13$, $-18 \leq k \leq 18$, $-18 \leq l \leq 618$	$-19 \leq h \leq 19$, $-4 \leq k \leq 4$, $-26 \leq l \leq 26$
Temperature	23 °C	23 °C
$2\theta_{\text{max}}$	55.0°	67.1°
Diffractometer	STOE IPDS II	STOE IPDS II
Mode of measurement	rotation method, $\varphi\Delta = 1^\circ$; 120 s per frame	rotation method, $\varphi\Delta = 2^\circ$; 120 s per frame
Reflections measured	7656	10,456
Independent reflections	1350	1386
Reflections $I > 2\sigma(I)$	837	807
Absorption correction	numerical; program XSHAPE [24]	numerical; program XSHAPE [24]
R_{int} , R_{sigma}	0.096, 0.059	0.089, 0.063
Absorption coefficient	29.72 mm^{-1}	33.33 mm^{-1}
Extinction coefficient [23]	0.00019(2)	0.0032(4)
Max./min. transmission	0.221; 0.098	0.281; 0.146
Structure solution	direct methods [23]	direct methods [23]
Refinement	SHELXL [23]	SHELXL [23]
Residual electron $e^-/\text{\AA}^3$	+0.93, -1.06, 0.24	+2.02, -1.67, 0.46
Min., max., sigma Weighting function [23]	0.029; 0.0	0.063; 0.0
Number of parameters	127	86
R-factors	$R_1(F) = 0.0284$; $wR_2(F^2) = 0.0590$	$R_1(F) = 0.0394$; $wR_2(F^2) = 0.1039$

4. Structure solutions

4.1. $Ni_{12}AlB_8$

A small single crystal was isolated from the sintered product and used for structure analysis. X-ray investigations with an image plate single crystal diffractometer (IPDS II, Fa. Stoe) revealed a C-centred orthorhombic unit cell with $a = 10.5265(16)$, $b = 14.527(2)$ and $c = 14.554(2) \text{ \AA}$. The reflection conditions led to the possible space groups *Aea2* (no. 41) and *Cmce* (no. 64). The solution of the structure was started in *Aea2* using direct methods (SHELXTL [23]). Because deviations from centrosymmetry were not significant the structure was transferred to the centrosymmetric space group *Cmce* and refined. Because of the possible formation of solid solutions all occupation factors were checked. It turned out that the metal sites have no deviations from an ordered occupation, but two of the boron atoms probably showed small deviations from full occupation (B3: 75(5)%, B6: 83(4)%) which were indicated by enlarged thermal displacement

Table 2
Coordinates, thermal displacement parameters (in \AA^2) and site occupation factors; esd's in parentheses.

Atom	x	y	z	$U_{\text{eq}}/U_{\text{iso}}^*$	sof**
<i>Ni_{10.6}Ga_{0.4}B₆</i>					
Ni1	0.5183(1)	0.25	0.66195(8)	0.0142(3)	1.009(10)
Ni2	0.3321(1)	0.25	0.75361(8)	0.0140(3)	1.010(9)
Ni3	0.7295(1)	0.75	0.84503(8)	0.0146(3)	1.006(10)
Ni4	0.4242(1)	0.75	0.55129(8)	0.0154(3)	0.990(10)
Ni5	0.7527(1)	0.75	0.46594(8)	0.0137(3)	0.997(10)
Ni6	0.9380(1)	0.75	0.54465(8)	0.0142(3)	1.002(10)
Ni7	0.5794(1)	0.25	0.89008(7)	0.0138(3)	1.003(10)
Ni8	0.5027(1)	0.75	0.78184(8)	0.0138(3)	0.999(10)
Ni9	0.6821(1)	0.75	0.69774(7)	0.0137(3)	0.990(10)
Ni10	0.7769(1)	0.25	0.58535(8)	0.0147(3)	1.002(1)
Ni/Ga	0.6156(1)	0.75	0.56445(7)	0.0134(3)	0.60(7)/0.40
B1	0.4016(10)	0.75	0.6755(7)	0.0154(21)*	1.04(5)
B2	0.3504(10)	0.25	0.6274(8)	0.0177(22)*	1.04(5)
B3	0.4250(11)	0.25	0.8591(7)	0.0190(23)*	1.03(5)
B4	0.3477(11)	0.75	0.8440(8)	0.0198(23)*	1.05(5)
B5	0.6298(10)	0.75	0.9660(8)	0.0183(22)*	1.02(5)
B6	0.6356(11)	0.25	0.7732(8)	0.0199(24)*	0.99(5)
<i>Ni₁₂AlB₈</i>					
Ni1	0.1316(1)	0.08147(7)	0.27947(7)	0.0143(2)	1.003(7)
Ni2	0.1343(1)	0.88797(7)	0.26813(7)	0.0150(2)	1.005(7)
Ni3	0.1294(1)	0.93093(7)	0.43474(7)	0.0158(2)	0.974(7)
Ni4	0.1338(1)	0.21647(7)	0.41192(7)	0.0143(3)	0.994(7)
Ni5	0.1319(1)	0.76365(7)	0.39561(7)	0.0142(3)	1.012(7)
Ni6	0.3319(1)	0.86774(7)	0.49804(7)	0.0145(3)	1.009(7)
Ni7	0.1676(1)	0.99086(8)	0.13201(7)	0.0139(3)	0.999(7)
Ni8	0.0	0.0762(1)	0.4205(1)	0.0146(3)	0.998(7)
Ni9	0.0	0.8629(1)	0.1245(1)	0.0136(3)	1.005(10)
Ni10	0.0	0.1171(1)	0.1304(1)	0.0139(3)	1.007(10)
Ni11	0.25	0.2362(1)	0.25	0.0138(3)	0.998(10)
Al1	0.0	0.2332(3)	0.2592(3)	0.0154(8)	1.004(22)
Al2	0.0	0.0	0.0	0.0142(9)	0.999(25)
B1	0.0	0.9887(8)	0.2069(7)	0.0081(20)*	1.06(4)
B2	0.0	0.9754(9)	0.3262(8)	0.0112(22)*	1.00(4)
B3	0.0	0.8594(12)	0.3596(13)	0.0265(35)*	0.75(5)
B4	0.0	0.8244(8)	0.4826(9)	0.0118(24)*	0.96(4)
B5	0.0	0.7059(8)	0.4971(9)	0.0098(21)*	0.98(4)
B6	0.7298(15)	0.0	0.5	0.0230(28)*	0.83(4)
B7	0.1900(9)	0.0750(6)	0.4193(6)	0.0133(15)*	0.95(3)
B8	0.2017(8)	0.1384(6)	0.1507(6)	0.0079(15)*	1.02(3)
B9	0.2878(8)	0.8453(6)	0.3568(6)	0.0132(18)*	0.92(3)

** In order to check for mixed occupations and/or vacancies site occupation factors were treated by turns as free variables at the end of the refinement. For the final least square cycle all values were fixed to unity (see text).

parameters assuming full occupation. For testing the boron site occupation factors the values for U_{eq} were fixed to be equal because of correlation effects. The final refinement was done with isotropic displacement parameters for boron to obtain smallest standard deviations. Furthermore a complete occupation of the boron sites was assumed because the underoccupation is not clearly proven (small electron number of boron, twinning/crystal quality). Finally R -values of $R_1(F) = 0.0284$ and $wR_2(I) = 0.0590$ were yielded with 1350 (837 with $I > 2\sigma(I)$) independent reflections and 127 free parameters.

Several crystals had to be checked because crystals of $Ni_{12}AlB_8$ are usually twinned resulting in a primitive tetragonal unit cell with $a = 14.52$ and $c = 10.53 \text{ \AA}$. The twinning is caused by the pseudotetragonal symmetry of the layers (see below).

4.2. $Ni_{12}GaB_8$

Crystals could be isolated from the crushed melt but turned out to be twinned. The tetragonal pseudo-cell indicated a close similarity to the Al-compound ($a = 14.53$ and $c = 10.56 \text{ \AA}$), but there were no suitable crystals for a satisfying refinement.

Table 3

Selected distances (in Å) and angles (in °); esd's in parentheses.

<i>Ni₁₂AlB₈</i>			
Ni1–B	2.128(9)–2.203(9) 5x	Ni6–B	2.029(5)–2.252(8) 5x
–Al	2.621(4)	–Al2	2.612(2)
–Ni	2.478(2)–2.816(2) 9x	–Ni	2.485(2)–2.991(2) 9x
Ni2–B	1.986(13)–2.221(9) 5x	Ni7–B	2.034(6)–2.190(8) 5x
–Al	2.685(4)	–Al2	2.612(1)
–Ni	2.492(2)–2.949(2) 9x	–Ni	2.504(2)–2.949(2) 9x
Ni3–B	2.026(12)–2.369(10) 7x	Ni8–B	2.000(9)–2.019(13) 4x
–Ni	2.495(2)–2.521(1) 6x	–Ni	2.478(2)–2.521(2) 8x
Ni4–B	2.128(9)–2.203(9) 5x	Ni9–B	2.029(5)–2.264(10) 4x
–Al	2.643(4)	–Al2	2.533(4)–2.694(4) 2x
–Ni	2.478(2)–2.820(2) 9x	–Ni	2.513(2)–2.8x
Ni5–B	1.986(13)–2.221(9) 5x	Ni10–B	2.034(6)–2.190(8) 4x
–Al	2.685(4)	–Al2	2.522(4)–2.548(4) 2x
–Ni	2.492(2)–2.991(2) 9x	–Ni	2.545(2)–2.625(2) 8x
		Ni11–B	2.088(9)–2.256(10) 4x
		–Al	2.635(1) 2x
		–Ni	2.492(2)–2.673(2) 8x
Al1–B	2.521(19)	Al2–B	2.418(16) 4x
–Ni	2.521(4)–2.686(4) 12x	–Ni	2.5489(2)–2.693(4) 12x
B1–B2	1.748(17)	B6–B7	1.811(11) 2x
–Ni	2.074(6)–2.221(9) 8x	–Ni	2.026(11)–2.034(5) 6x
B2–B1/B3	1.748(22)/1.753(22)	–Al2	2.419(16)
–Ni	2.008(13)–2.183(9) 7x	B7–B6/B8	1.811(11)/1.785(13)
B3–B2/B4	1.753(22)/1.860(22)	–Ni	2.000(9)–2.219(9) 7x
–Ni	1.986(13)–2.035(14) 6x	B8–B7	1.785(13)
–Al1	2.520(18)	–Ni	2.076(13)–2.262(9) 8x
B4–B3/B5	1.860(22)/1.734(17)	B9–Ni	2.089(9)–2.369(10) 9x
–Ni	2.073(9)–2.176(10) 7x	B7–B6–B7	124.4(10)
B5–B4	1.734(17)	B6–B7–B6	121.2(3)
–Ni	2.068(6)–2.260(13) 8x		
B1–B2–B3	112.5(9)		
B2–B3–B4	122.0(11)		
B3–B4–B5	112.9(9)		
<i>Ni_{10.6}Ga_{0.4}B₆</i>			
Ni1–B	2.071(9)–2.375(14) 4x	Ni6–B	2.152(10)–2.363(12) 6x
–Ga/Ni	2.515(2) 2x	–Ni	2.534(2)–2.949(1) 10x
–Ni	2.515(2)–2.949(1) 9x	Ni7–B	1.976(14)–2.099(14) 4x
Ni2–B	2.116(13)–2.452(15) 7x	–Ni	2.431(2)–2.949(1) 9x
–Ni	2.502(2)–2.949(1) 10x	Ni8–B	2.177(15)–2.212(11) 6x
Ni3–B	2.026(12)–2.369(10) 7x	–Ni	2.515(2)–2.949(2) 9x
–Ni	2.495(2)–2.984(2) 11x	Ni9–B	2.029(10)–2.159(15) 3x
Ni4–B	2.118(12)–2.155(9) 3x	–Ga/Ni	2.398(2)
–Ga/Ni	2.364(2)–2.499(1) 3x	–Ni	2.502(2)–2.949(1) 10x
–Ni	2.646(2)–2.949(1) 8x	Ni10–B	2.044(14)–2.324(13) 4x
Ni5–B	2.024(13)–2.967(9) 3x	–Ga/Ni	2.497(2) 4x
–Ga/Ni	2.372(2)	–Ni	2.519(2)–2.949(1) 9x
–Ni	2.431(2)–2.949(1) 10x	Ga/Ni–Ni	2.363(2)–2.513(2) 9x
–Ga/Ni			2.949(1) 2x
B1–B2	1.792(10) 2x	B3–B4	1.766(11) 2x
–Ni	2.075(9)–2.194(12) 7x	–Ni	1.982(14)–2.000(12) 7x
B2–B1	1.792(10) 2x	B4–B3	1.766(11) 2x
–Ni	2.031(13)–2.160(12) 7x	–Ni	2.093(10)–2.190(14)
B1–B2–B1	110.2(9)	B3–B4–B3	112.9(11)
B5–Ni	2.055(9)–2.395(14) 9x	B6–Ni	2.034(10)–2.461(15) 9x

4.3. *Ni_{10.6}Ga_{0.4}B₆*

A small crystal fragment was isolated from the solidified melt and measured on a single crystal diffractometer (IPDS II). According to the reflection conditions possible space groups were *Pna2₁* (no. 33) and *Pnma* (no. 62). The solution with direct methods was started in *Pnma* and yielded in a model with 11 metal positions and 6 boron sites. Assuming complete occupation by Ni and B, respectively, all boron sites were nearly equal, but one of the metal sites (Ni11) showed a slightly reduced displacement parameter. With a free site occupation factor the value was 104.3(9)%. The occupation with Ga resulted in 91.8(8)%. Because EDXS measurements revealed a Ga-content of 4% and this site is only coordinated by Ni (see discussion) a mixed occupation

Ni/Ga was assumed and refined (60(7)% Ni and 40(7)% Ga). Again, boron atoms were refined with isotropic displacement parameters. Finally *R*-values of *R*₁(*F*)=0.0394 and *wR*₂(*I*)=0.1039 were obtained with 1386 (807 with *I* > 2σ(*I*)) independent reflections and 86 free parameters.

Tables 1–3 contain measure parameters and data on the refinements. Further details may be obtained from: (Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) (fax: +49 724-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the registry number CSD-421553 (Ni₁₂AlB₈) or CSD-421554 (Ni_{10.6}Ga_{0.4}B₆).

5. Results and discussion

The crystal structures of Ni₁₂AlB₈ and Ni_{10.6}Ga_{0.4}B₆ represent new structure types, which both show the typical elements of transition metal borides. All boron atoms are coordinated as three-fold capped trigonal prisms of transition metal. Capping atoms are boron, transition metal and main group metal as well. For the case of boron oligomers or chains are formed. The difference between transition metal and main group metal is clearly seen in the number of boron bonds, none for Ga in Ni_{10.6}Ga_{0.4}B₆, one, respectively, two for Al or Ga in Ni₁₂AlB₈ and Ni₁₂GaB₈.

5.1. *Ni₁₂AlB₈*

The crystal structure of Ni₁₂AlB₈ can be described by alternating layers stacked along [1 0 0]. Layers at *x*=0 and *x*=1/2 (Fig. 2a) consist of B₅ unit as a fragment of a zig-zag chain. The orientations of the chain fragment are [0 1 1] and [0 1 $\bar{1}$], respectively. The boron atoms are located exactly on the mirror planes at *x*=0 and *x*=1/2. The central B-atom (B3) is capped by Al1, the others free rectangular planes are capped by Ni-atoms (Ni8, Ni9 and Ni10). Al2 is located between four B₅-units. The second layer (Fig. 2b) at *x*=1/4 and *x*=3/4 contains B₅-units, too, and additionally isolated boron atoms (B9). The orientation is again in directions [0 1 1] and [0 1 $\bar{1}$], but the units itself are rotated by ±90° compared to the layers on the mirror plane. Again, the trigonal prism of the central boron (B6) is capped by Al (Al2) while the others are capped by Ni (Ni8, Ni10 and Ni11).

The two different B₅ units shown in Fig. 3 are very similar but exhibit small differences. According to the site symmetry of the unit cell the symmetry is C_s for the units on the mirror plane and C₂ for the units on *x*=±1/4. But the deviations from C_{2v}-*mm*2 are quite small. The B–B distances between 1.73 and 1.86 Å correspond the usual values of a B–B single bond (*r*_B=0.89 Å [25]) and agree well to the values in binary and ternary borides [4,8]. Ni–B distances of the trigonal prisms are between 1.99 and 2.26 Å. In both cases the Ni–B distances to the capping atom Ni8 are remarkably short (2.00–2.02 Å). The B–B distances are slightly different but within the usual range.

All the Ni-atoms have contacts to B atoms. Most of them have 4 or 5 boron neighbours. Surrounding is completed by 8 or 9 Ni atoms and 1 or 2 Al atoms. Exceptions are Ni3 with 7 boron and 6 Ni atoms and Ni8 with quite short bonds to 4 boron and 8 Ni-atoms. This results from the special situations. Ni3 forms the common edge of the central trigonal prism BNi₆ in both of the B₅ units. Ni8 caps all the four intermediate trigonal prisms. In general Ni–B and Ni–Ni distances agree well to the values of binary Ni borides with trigonal prisms (Ni₃B: Ni–B: 6 × 2.034–2.255, 2 × 2.293, 2.613 and Ni–Ni: 11 × 2.454–2.743 Å, [26]).

Al is mainly coordinated by Ni but shows contacts to B, too. For Al1 and Al2 the Ni-atoms form a cuboctahedron (Fig. 3) in which one (Al1–B: 2.52 Å) or two (Al2–B: 2.42 Å) of the square planes are

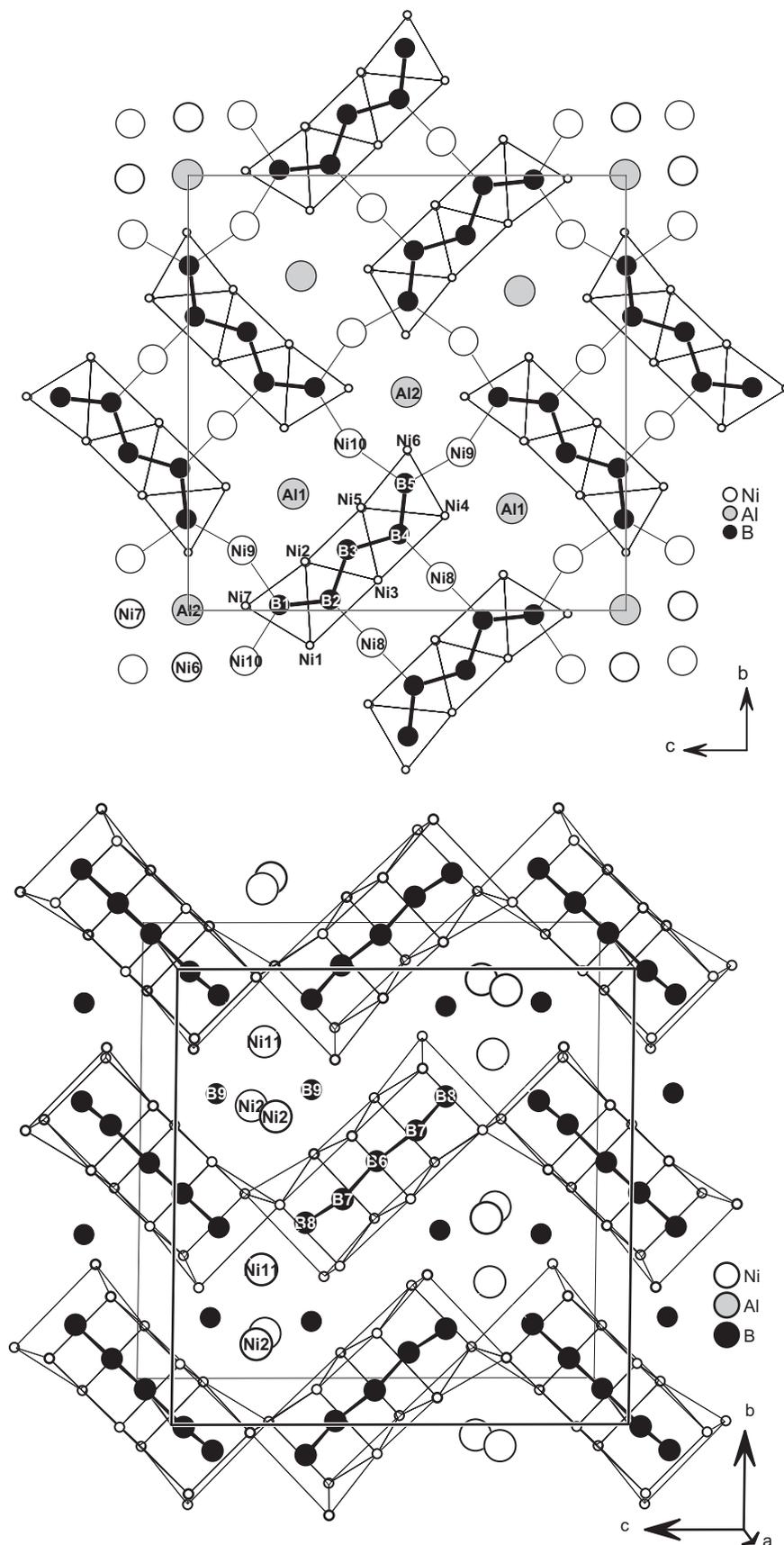


Fig. 2. Structure of $\text{Ni}_{12}\text{AlB}_8$; (a) layers with B_5 units and Al atoms at $x=0$ and $x=1/2$ and (b) layers of B_5 units and isolated B atoms at $x=1/4$.

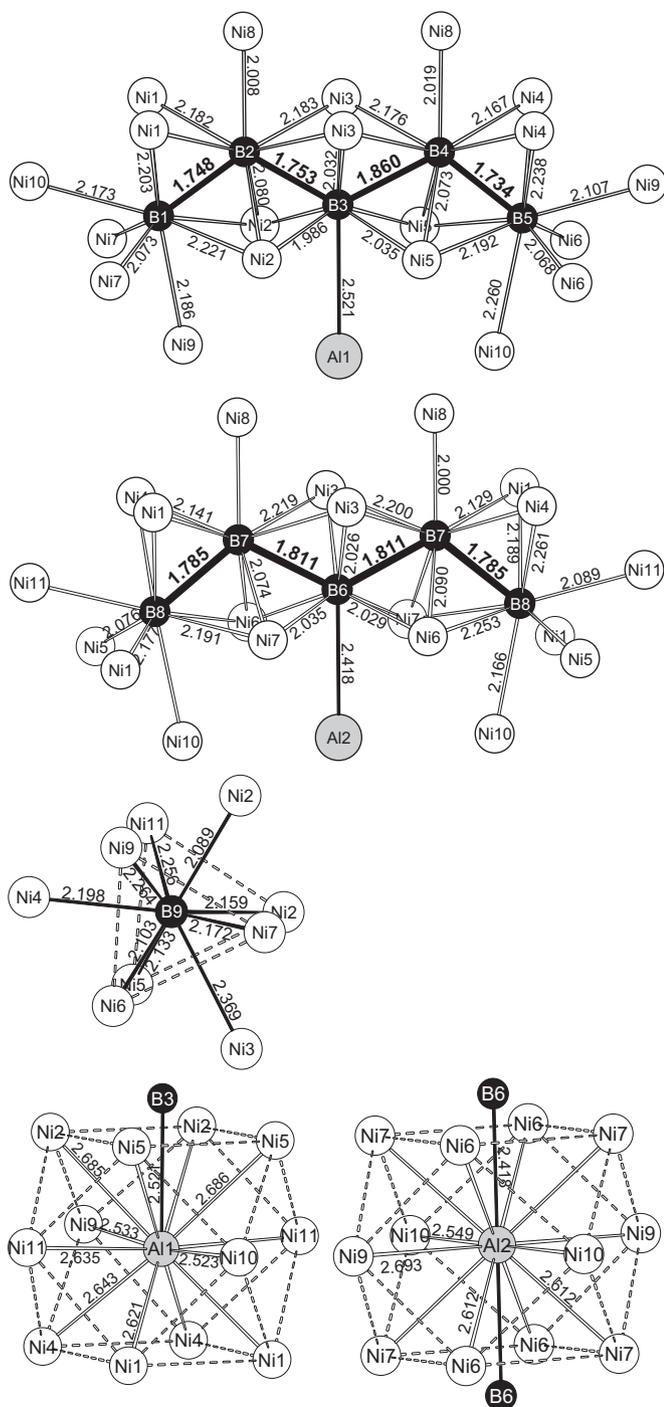


Fig. 3. Coordination polyhedra in $Ni_{12}AlB_8$.

capped by boron. According to the high coordination number the Al–B distances are longer than in binary AlB_2 : 2.378 Å [27] and ternary Al borides (Cr_2AlB_2 : 2.276 Å [28], Mn_2AlB_2 : 2.316 Å [29] and Fe_2AlB_2 : 2.286 Å [30]).

According to the results of the refinement the central position of the B_5 unit might be partially empty. Because of the low electron number of boron, the uncertainty is quite high, but there are several other examples for a deficit on a boron site in similar compounds like Ru_2ZnB_{2-x} [31] or $ZrIr_3B_{4-x}$ [32].

The reason for the twinning of $Ni_{12}AlB_8$ and $Ni_{12}GaB_8$ is obvious from Fig. 2. The layers at $x=0$ and $x=1/2$ have a tetragonal pseudo-symmetry. The second type of layers at $x=$

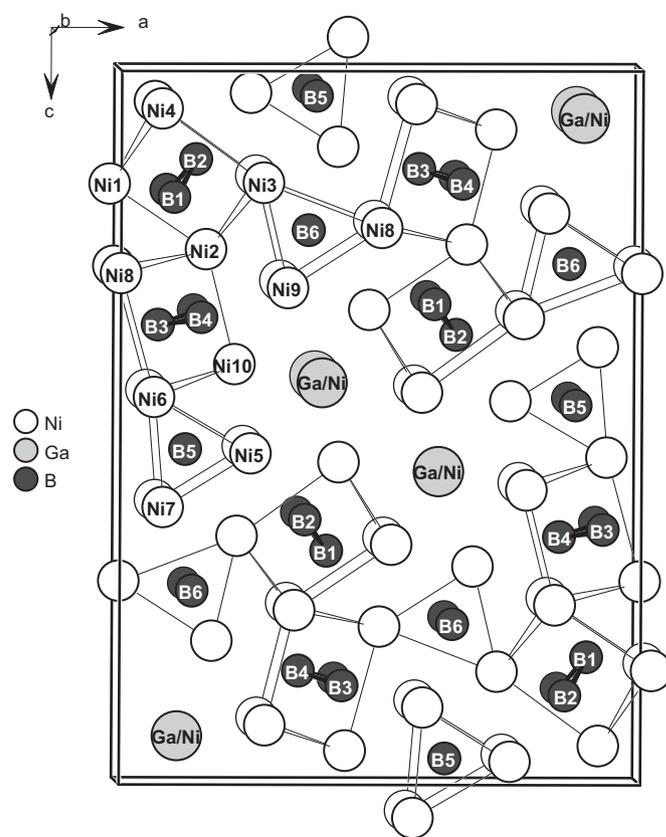


Fig. 4. Structure of $Ni_{10.6}Ga_{0.4}B_6$, projection in direction [0 1 0].

$\pm 1/4$ can be rotated by 90° without important structural changes. Therefore the orientation of this layer, which makes the difference between the two nearly equal directions y and z , is not clearly defined. In general a tetragonal modification with enlarged (double or fourfold) lattice parameters might be possible as it is known for the monoborides MoB and WB [33] where the orientation of the zig-zag chains is different (orthorhombic form: parallel; tetragonal form: orthogonal).

5.2. $Ni_{10.6}Ga_{0.4}B_6$

The crystal structure of $Ni_{10.6}Ga_{0.4}B_6$ is shown in Fig. 4 as a projection in direction [0 1 0]. Similar to $Ni_{12}AlB_8$ the surroundings of all boron atoms are trigonal prisms BNi_6 with the rectangular planes capped by B or Ni atoms. Two of the six independent B atoms (B_5 and B_6) are coordinated only by Ni, thus forming trigonal prisms BNi_6Ni_3 with the threefold axis parallel to [0 1 0]. The trigonal prisms of the remaining B atoms are linked by two common faces and build up two different zig-zag chains (B_1/B_2 and B_3/B_4) running parallel to the b -axis. The trigonal prisms of the zig-zag chain are linked by a common Ni atom (Ni_2). The capping Ni atom of the chain with B_1/B_2 (Ni_8) comes from the other chain while the capping Ni atom of the chain with B_3/B_4 is from the isolated one of the isolated prisms (Ni_9). The position which obviously contains gallium has no direct contacts to boron.

The atoms' surroundings (Fig. 4) reflect this building principle of B–B zig-zag chains and isolated trigonal prisms BNi_6Ni_3 . All the B atoms have coordination number CN 9. For B_1/B_2 and B_3/B_4 there are B–B distances of 1.792 and 1.766 Å, respectively. These values are typical for monoborides (CrB : 1.789 Å [34] and FeB :

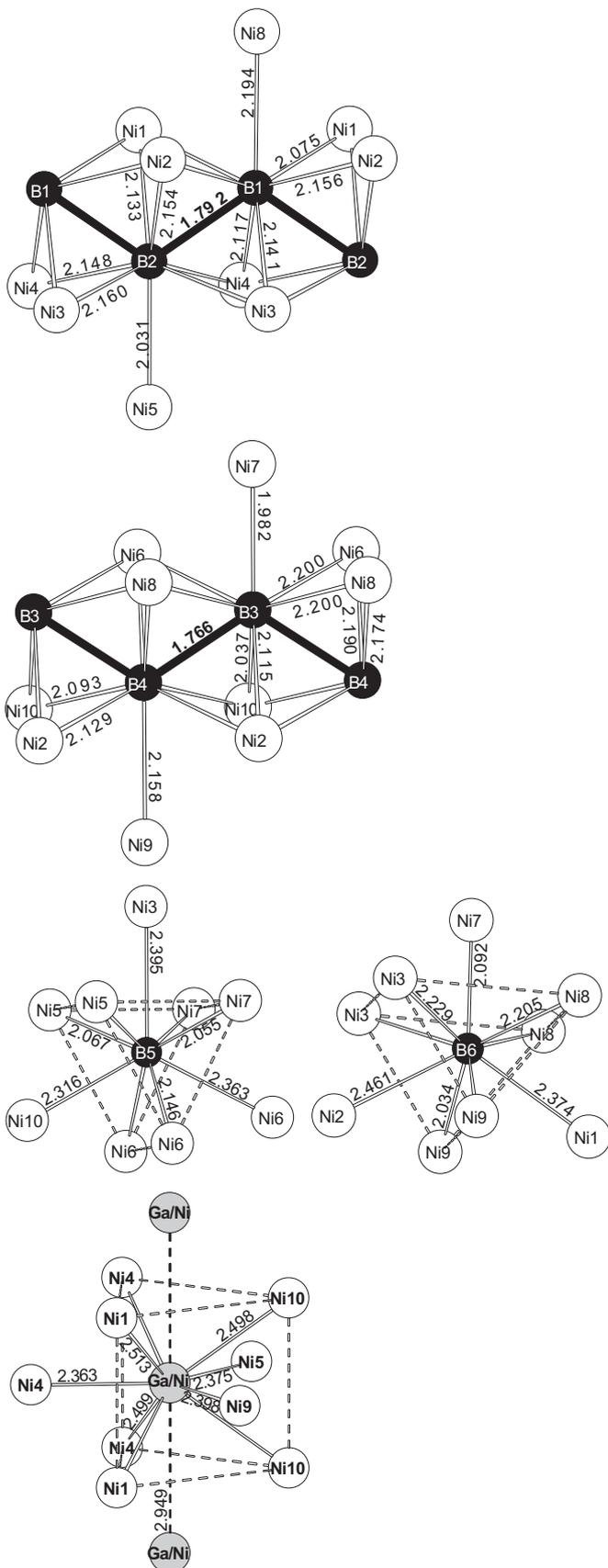


Fig. 5. Coordination polyhedra in $\text{Ni}_{10.6}\text{Ga}_{0.4}\text{B}_6$.

1.785 [35]) and also comparable to ternary borides containing zig-zag chains (Cr_2AlB_2 : 1.762 [28], Mn_2AlB_2 : 1.72 [29] and Fe_2AlB_2 : 1.74 Å [30]). Sections of the chains are shown in Fig. 5. The Ni–B

distances vary between 1.982 and 2.200 Å. Similar values are found in other binary Ni borides [4,10]. The isolated prisms of B5 and B6 are slightly distorted. The differences can be explained by the interaction with the polyhedra of the zig-zag chains. Shorter distances are observed for Ni atoms which serve as capping atoms (Ni5, Ni7, Ni9). All Ni atoms have bonds to boron. According to the position in the framework of condensed BNi_6 trigonal prisms this number ranges from 3 (Ni4, Ni5, Ni9) over 4 (Ni1, Ni7, Ni10) and 6 (Ni3, Ni6, Ni8) to a maximum of 7 (Ni2). The coordinations of Ni are completed by 9–11 metal atoms (< 3 Å).

The site with the mixed Ni/Ga occupation shows CN 11 exclusively formed by metal atoms. The polyhedron can be described as a trigonal prism of Ni atoms (2.498–2.513 Å) with 3 Ni atoms capping the rectangular planes (2.363–2.398 Å) and two mixed sites capping the trigonal planes (2.949 Å). The tendency of Ga to avoid direct contacts to boron is clearly seen in the non-existence of binary borides of gallium and in the crystal structures of the few known ternary borides ($\text{Ir}_9\text{Ga}_{2.7}\text{B}_5$, $\text{Pt}_9\text{Ga}_3\text{B}_4$ [36], $\text{Ir}_4\text{Ga}_8\text{B}$ [37], $\text{Co}_{21.9}\text{Ga}_{1.1}\text{B}_6$ [38] and $\text{Ni}_{20}\text{Ga}_3\text{B}_6$ [16]).

The crystal structure of $\text{Ni}_{10.6}\text{Ga}_{0.4}\text{B}_6$ is closely related to the structures of the binary Ni_4B_3 . Rundquist and Pramatus [10] have described an orthorhombic form with two different B–B zig-zag chain (B–B distances 1.73 and 1.89 Å, respectively) and two isolated B atoms with a trigonal-prismatic coordination. The monoclinic variant shows only one type of zig-zag chain. Within this chain one B atoms has a linear coordination (1.85 Å), the other a bent one (1.92 Å, 114°). In contrast to $\text{Ni}_{10.6}\text{Ga}_{0.4}\text{B}_6$ all Ni atoms have contacts to boron with Ni–B distances between 2.04 and 2.42 Å.

In the course of investigations on ternary Ni borides with ternary rare earth metals Kuzma et al. confirmed the existence of the binary borides NiB , Ni_4B_3 , Ni_2B and Ni_3B [39]. There were no hints for the existence of a binary Ni-boride with a composition Ni_{11}B_6 [40].

5.3. $\text{Ni}_{12}\text{GaB}_8$

According to the X-ray investigations $\text{Ni}_{12}\text{GaB}_8$ is isotopic to $\text{Ni}_{12}\text{AlB}_8$. The lattice parameters are slightly enlarged according to the greater volume of Ga in intermetallics [2]. The intensities of the X-ray pattern calculated with the atomic parameters of $\text{Ni}_{12}\text{AlB}_8$ exhibited excellent agreement. In the system Ni/Ga/B it represents the second ternary compound besides the τ -boride $\text{Ni}_{20}\text{Ga}_3\text{B}_6$ [18,19]. Furthermore it is one of the very few Ga-containing borides. The τ -borides were already mentioned. Jung and co-workers have characterised the compounds $\text{Ir}_9\text{Ga}_{2.7}\text{B}_5$, $\text{Pt}_9\text{Ga}_3\text{B}_4$ [36] and $\text{Ir}_4\text{Ga}_8\text{B}$ [37]. These compounds show very long distances Ga–B ($\text{Ir}_4\text{Ga}_8\text{B}$: 2.82, $\text{Ir}_9\text{Ga}_{2.7}\text{B}_5$: 2.65 and $\text{Pt}_9\text{Ga}_3\text{B}_4$: 2.89 Å). Using the coordinates of $\text{Ni}_{12}\text{AlB}_8$ the Ga–B distances in $\text{Ni}_{12}\text{GaB}_8$ can be calculated to 2.42 and 2.52 Å. They represent the shortest distances ever found. Nevertheless even this distance is quite long compared to the sum of the atomic radii [25].

Because Kuzma and co-workers [16] made no definite characterisation of the ternaries $\text{Ni}_8\text{AlB}_{11}$ and Ni_5AlB_4 we cannot decide whether $\text{Ni}_{12}\text{AlB}_8$ represents one of these phases or not. The equilibrium phases were investigated between 800 and 1000 °C. In the course of our investigations it turned out that around 800 °C there is the formation of other ternary phases which are not $\text{Ni}_{12}\text{AlB}_8$.

$\text{Ni}_{12}\text{GaB}_8$ might be the phase which was described by Stadelmeyer and co-workers [18]. They had investigated the equilibrium phases of the Ni-rich field at 800 °C. Besides the τ -boride they have found a second ternary phase with an estimated composition Ni_6GaB_3 but gave no further details. A similarity of $\text{Ni}_{12}\text{GaB}_8$ to the compound $\text{Ni}_{12}\text{GaB}_7$, that was mentioned by Chaban and Kuzma [19] (oc , $a=7.05$, $b=7.75$ and $c=10.67$ Å) but not characterised, cannot be seen.

6. Conclusions

The structures of $\text{Ni}_{12}\text{AlB}_8$, $\text{Ni}_{12}\text{GaB}_8$ and $\text{Ni}_{10.6}\text{Ga}_{0.4}\text{B}_6$ are further examples for the pronounced tendency in transition metal borides to form B–B bonds. For borides with a ratio M:B between 2 and 1 there is a transition from B–B zig-zag chains via oligomeric units (B_2 , B_3 , B_4 and B_5) to isolated boron atoms. Different ratios can be realized by combination of isolated atoms with chains like in $\text{Ni}_{10.6}\text{Ga}_{0.4}\text{B}_6$, or with oligomeric units like in $\text{Ni}_{12}\text{AlB}_8$ and $\text{Ni}_{12}\text{GaB}_8$. The latter represent the first example for a pentameric B_5 unit. Threefold capped trigonal prisms BM_6 are by far the most common structural units. Chains and oligomeric units are built up by sharing common rectangular planes which allows the formation of direct B–B bonds with a typical length of 1.75–1.80 Å. The tendency of the late transition metals to form bonds to boron is well developed. The combination of late transition metals with other metals of lower affinity to boron in ternary compounds is clearly seen in the structural motifs. For Al in $\text{Ni}_{12}\text{AlB}_8$ the Al atoms have only one or two quite long distance to boron (2.59 and 2.47 Å, respectively) in addition to a cuboctahedral coordination by metal atoms. Ga in $\text{Ni}_{10.6}\text{Ga}_{0.4}\text{B}_6$ completely avoids direct contacts to boron.

Because of the high technological importance of Ni/Al-based superalloys [1d,e] Campell and Kattner [41] have investigated the thermodynamic stability of binary and ternary compounds in the system Ni/Al/B. According to their data the boron-rich τ -boride $\text{Ni}_{20}\text{AlB}_{14}$ is not stable. This is confirmed by our observation that $\text{Ni}_{20}\text{AlB}_{14}$ is formed from a metallic melt at 1250 °C on cooling, but it transforms to $\text{Ni}_{12}\text{AlB}_8$ by annealing between 900 and 950 °C.

The formation of the ternary compounds seems to be favoured at lower temperatures. For $\text{Ni}_{12}\text{AlB}_8$ and $\text{Ni}_{12}\text{GaB}_8$ it was essential to keep the samples at temperatures about 900 °C. This is a general problem for the appearance of new ternary compounds in systems with high-melting components, which cannot be obtained directly from a melt with corresponding composition. The formation is hindered at lower temperatures by kinetic reasons while at higher temperatures the compounds start to decompose to other solid phases. Therefore synthesis, characterisation, preparation of phase-pure samples, and crystal growth are difficult to control and the “synthetic window” can be very small and sometimes accidentally.

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