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Single crystal studies on Co-containing τ-borides $Co_{23-x}M_xB_6$ (M = Al, Ga, Sn, Ti, V, Ir) and the boron-rich τ-boride $Co_{12.3}Ir_{8.9}B_{10.5}$

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ABSTRACT

Single crystals of the cubic τ-Borides $Co_{23-x}M_xB_6$ (M = Al, Ga, Sn) were synthesised from the elements at temperatures between 1200 and 1500 °C. According to the structure refinements one (Ga, Sn: 8*c*) or two (Al: 4*a* and 8*c*) of the four independent metal sites show a mixed occupation Co/M resulting in the compositions $Co_{20.9}Al_{2.1}B_6$, $Co_{21.9}Ga_{1.1}B_6$, and $Co_{21.4}Sn_{1.6}B_6$, respectively. Melts with Indium gave access to $Co_{23}B_6$ as the first binary τ-boride ($Fm\overline{3}m$, $a = 10.4618(13)$ Å, 104 refl., 14 param., $R_1(F) = 0.0132$, $wR_2(F^2) = 0.0210$). With M = Ir mixed occupations occur for all sites and the boron content varies. The composition for the boron-poor single crystal was $Co_{16.2}Ir_{6.8}B_6$. A higher Ir-content enables the uptake of additional boron resulting in a composition $Co_{12.3}Ir_{8.9}B_{10.5}$. This can be explained be the substitution of metal atoms on the 8*c*-site by B_4-tetrahedra. A boron-rich phase was observed for the first time for a τ-boride of cobalt. All compositions were confirmed by EDX measurements.

1. Introduction

Metal rich borides of 3*d* transition metals with a M:B ratio >2 play an important role in hardening processes of alloys. They are formed on the surface by boridising (for example with gaseous BCl_3) or between the grain boundaries of the alloys by segregation. The so-called τ-borides with a composition $M_{23}B_6$ are the most numerous representatives of metal rich borides. Up to now more than 80 representatives are known [1]. Its crystal structure belongs to the $Cr_{23}C_6$ type [2] which contains four different metal sites (48*h*, 32*f*, 4*a*, 8*c*, see below). As pointed out by Stadelmaier [3] τ-borides are typically ternary borides with a 3*d* metal (Cr–Ni) on the sites 48*h* and 32*f* while the sites 4*a* and 8*c* are occupied by rare earth metals, 4*d* and 5*d* transition metals or a main group metal. Because binary τ-borides were unknown the minor component was called "τ-stabilizer". It was known that mixed occupation occurs for the different metal sites according to the different size [3,4] but usually a full occupation of the sites 4*a* and/or 8*c* is assumed to reach the ideal compositions $M_{22}M'B_6$, $M_{21}M'_2B_6$ and $M_{20}M'_3B_6$ with M' as τ-stabilizer.

Most of the investigations were done on powder samples for several reasons. Firstly τ-borides were usually investigated in the course of equilibrium studies. For this the samples were heated up for a short time near the assumed melting point and then annealed at temperatures between 800 and 1000 °C [3,4]. The resulting products were normally characterized only by metallographic methods and X-ray powder diffraction. Secondly, the formation of single crystals is difficult because of kinetics reasons as meting points and retain temperatures are very different. Therefore only a few detailed investigations of the formation of solid solutions in τ-borides on the basis of single crystal data are reported.

A new aspect started up, when it was shown for the τ-borides of the system Ni/Al/B [5] that the enlargement of the boron content is caused by the substitution of aluminium on site 8*c* by B_4-tetrahedra. This was the first example for a B_4-tetrahedron in a solid state compound. Besides this there is also a mixed occupation of site 4*a* by Al and Ni. Therefore the formation of solid solutions is described by two different mechanisms: $Ni_{20}(Al_{1-x}Ni_x)(Al_{1-y}B_{4y})B_6$. Representatives are $Ni_{20.5}Al_{2.5}B_6$ (a = 10.486 Å), $Ni_{20}Al_3B_6$ (a = 10.511 Å) and $Ni_{20}AlB_{14}$ (a = 10.617 Å). The enlargement of the lattice parameter with rising B-content is explained by the higher volume of a B_4-tetrahedron. Besides the use of excess Al played a central role for the formation and crystallisation of the boron-rich τ-boride. Because the differences of the diffraction patterns are very small, the use of single crystal data is essential for unambiguous results. In continuation it

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turned out that in Ni-containing τ-borides several other main group metals (M' = Ga, Sn) are able to stabilise boron-rich τ-phases with B_4-tetrahedra [6,7]. Furthermore it was shown that iridium can substitute larger amounts (i.e. $x>3$) of the 3*d*-metal ($Cr_{7.9}Ir_{14.1}B_6$ [8], $Fe_{10.0-15.4}Ir_{13.0-7.6}B_6$[4]) and, additionally, forms a boron rich τ-boride ($Ni_{12.4}Ir_{10.6}B_{11.8}$ [6]).

Because of the similarity of Ni and Co, for example Hirota has described a solid solution $(Ni,Co)_{20}Al_3B_6$ [17], we have investigated analogous τ-borides with cobalt. τ-stabilizers M' were iridium and the main group metals Mg, Al, Ga, In, and Sn. The first boron rich τ-boride of cobalt was obtained for M' = Ir. M' = Mg, Al, Ga, and Sn resulted in boron-poor τ-phases with M′ mainly located on site 8*c*. By use of an In-melt we were able to synthesise and characterize single crystals of $Co_{23}B_6$ as the first binary τ-boride. Furthermore we yielded the first boron rich τ-boride of cobalt, $Co_{12.3}Ir_{8.9}B_{10.5}$, where the additional boron content is realized by the incorporation of B_4 tetrahedra.

2. Experimental

2.1. Syntheses and characterisation

The elements were mixed in ratios, which covers different amount of M' and boron. They were pressed into pellets (mass: ~300 mg) and put into a corundum crucible. Under an atmosphere of argon the pellets were heated up to a maximum temperature (1200–1450 °C) followed by a dwell time of several hours (1–10 h) and cooling down (rate: 10–15 °C/h) to a medium temperature (600–1000 °C). Then the furnace was turned off. Further investigations were done with the crushed metallic reguli. Table 1 gives an overview of the samples prepared.

Powdered samples were characterized by XRD (STOE, Darmstadt, Germany, STADI-P, transmission geometry; Mo*K*α-radiation and linear PSD or Cu*K*α-radiation and IP-detector).

Single crystal investigations and data collections were performed by using a single crystal diffractometer (STOE, Darmstadt, Germany, IPDS II, Mo*K*α-radiation, graphite monochromator) equipped with an image plate detector.

EDX measurements (Electron microscope: Zeiss DSM-960; EDX-system: Link/LEO 1525) were usually made of the crystals which were already used for the structure determinations (see below). The irregular shape of the crystals can cause problems for a reliable determination of the Co/Ir-ratio. Therefore data were selected from regions where the evaluation of Ir–M-series and Ir–L-series resulted in the same compositions. By comparison to compounds with known composition the errors can be estimated to be ±1 at%. In some cases additional analyses were done by WDX measurements (CAMECA SX 100). They confirmed the results for Co and Ir. In contrast to several other cases (for example $Li_2B_{12}C_2$ [9], $MgB_{12}C_2$ [10], $MgB_{12}Si_2$ [11]) the unfavourable crystal shape prevented to obtain reliable data for the boron content.

Co/Mg/B: In order to avoid the loss of Mg the samples were enclosed in a tantalum ampoule. The main product was Co_2B. The additional reflections were assigned to a τ-phase. A refinement of the τ-phase reflections resulted in a lattice constant of $a = 10.560(2)$ Å.

Co/Al/B: τ-borides were obtained for compositions between $Co_{22}AlB_6$ ($a = 10.474(7)$ Å) and $Co_{21}Al_2B_6$ ($a = 10.495(2)$ Å). Attempts to synthesise boron-rich τ-borides yielded in CoB as main product and Co_2B and CoAl as a by-product.

Co/Ga/B: A single phase τ-boride with $a = 10.5041(4)$ Å was obtained from samples with a composition $Co_{22}GaB_6$. The range of homogeneity is quite narrow. There is no evidence for the existence of Ga-rich and/or boron-rich τ-phases.

Co/Sn/B: Syntheses were done at maximum temperature of 1450 °C. The formation of a τ-boride was only observed for boron-poor samples. The variation of the ratio Co/Sn did not result in a significant change of the lattice parameter (10.594(11) Å–10.597(10) Å). By-products were $CoSn_2$ and Co, respectively. Syntheses with high boron content did not yield a τ-phase but the formation of Co_2B and CoB.

Co/In/B: XRD of powdered samples showed for the composition $Co_{22}InB_6$ the formation of a τ-boride with $a = 10.553(2)$ Å. In the range between $Co_{22.5}In_{0.5}B_6$ and $Co_{22.6}In_{0.4}B_6$ all reflections were assigned to a τ-boride. The refinement of the lattice parameters resulted in values of 10.4673(16) Å and 10.476(2) Å, respectively. Experimental and calculated diffraction patterns are in excellent agreement (Fig. 1). With lower In-content no τ-phase was observed and Co_3B was the main product besides unreacted Co. All efforts to synthesise $Co_{23}B_6$ from the melt failed and resulted in samples with different amounts of Co_3B, Co_2B and Co.

Investigations by EDX confirmed the absence of indium in the single crystals used for the structure refinements (see below).

Co/Ir/B: τ-phases were observed for boron-poor and boron-rich samples. While the composition's variation was quite small for the first ($Co_{15}Ir_8B_6$: 10.840(8) Å) it was significantly larger for the latter ($Co_{16}Ir_7B_{15}$: 10.863(2) Å, $Co_9Ir_{14}B_{15}$: 11.043(7) Å). The maximum Co/Ir substitution can be estimated to about 50% because higher amounts of Ir resulted in the formation of $IrB_{1.1}$ and $Co_{7-x}Ir_xB_3$ (Re_7B_3-type, [12]). No τ-phases were obtained for samples with a lower Ir-content, i.e., $x \approx 3$.

2.2. Single crystal investigations and refinements

Single crystals were isolated from the crushed melt and investigated with a single crystal diffractometer (STOE IPDS II, image plate detector, Mo*K*α-radiation). The indexing routine revealed a face-centred cubic unit cell in each case. Lattice parameters (10.46–10.95 Å) and reflection conditions were characteristic for τ-borides. The datasets were corrected for absorption and merged in Laue-class $m\overline{3}m$. The subsequent refinements were started with the known structure model of a τ-boride. Because mixed occupations were expected all site occupation factors were checked. Mixed occupations were considered, if the deviations were greater than triple of the (usually very small) standard deviations. For all systems several single crystals were measured leading to very similar results. The best results were used for the discussion. Further details are listed in Tables 2, 3, and 4, or 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 numbers CSD-419739 ($Co_{20.9}Al_{2.1}B_6$), CSD-419740 ($Co_{21.4}Sn_{1.6}B_6$), CSD-419736 ($Co_{21.9}Ga_{1.1}B_6$), CSD-419735 ($Co_{23}B_6$), CSD-419734 ($Co_{16.2}Ir_{6.8}B_6$), CSD-419741 ($Co_{12.3}Ir_{8.9}B_{10.5}$).

$Co_{20.9}Al_{2.1}B_6$: Al was localised on site 8*c* according to the Difference Fourier synthesis. Furthermore a small amount of Al was attributed to the site 4*a* because the value of the displacement parameter was implausible for an occupation only by Co (EDX: Co: 91%, Al: 9%).

$Co_{21.4}Sn_{1.6}B_6$: A single crystal was isolated from a boron-poor melt with a nominal composition $Co_{20}Sn_3B_6$. Sn was only localised on site 8*c* according to difference Fourier synthesis. (EDX: Co: 93%, Sn: 7%).

$Co_{21.9}Ga_{1.1}B_6$: Because of the smaller difference of the electron numbers the localisation of Ga is more difficult. Difference Fourier syntheses and refinements of the site occupation factors showed an enlarged electron number only on site 8*c*. The assumption of a

Table 1
Experimental conditions and results of XRD characterisation of τ-borides Co/M/B (M = Al, Ga, Sn, Ir).

System/sample composition	Maximum temperature/holding time	Cooling rate	Lower holding temperature	τ-phase powder	τ-phase, single crystal	By-products, main part in **bold** traces as $\gg$
Co/Ga/B						
$Co_{20}Ga_3B_6$	1450 °C/10 h	10 °C/h	900 °C	10.4976 (11)		$\gg$Co
$Co_{22}GaB_6$	”	”	”	10.5041 (4)	10.484 (2)	Single phase
$Co_{17}Ga_6B_6$	”	”	”			$\mathbf{Co_2B}$, CoGa,
$Co_{13}Ga_{10}B_6$	”	”	”			**CoGa**, CoB
$Co_{20}Ga_3B_{12}$	”	”	”	10.4978 (6)		Co_2B
$Co_{13}Ga_{10}B_{12}$	”	”	”			$\mathbf{CoGa_3}$, Co_2B
$Co_{13}Ga_{10}B_{15}$	”	”	”			**CoB**, Ga
Co/Al/B	1500 °C/1 h	15 °C/h	900 °C			
$Co_{22.5}Al_{0.5}B_6$	”	”	”			**Co**, Co_2B, AlCo
$Co_{22}AlB_6$	”	”	”	10.474 (7)		Co_3B
$Co_{21}Al_2B_6$	”	”	”	10.495 (2)	10.482 (2)	Co_2B
$Co_{20}Al_3B_{15}$	”	”	”			**CoB**, Co_2B, AlCo
$Co_{19}Al_4B_{15}$	”	”	”			**CoB**, Co_2B, AlCo
$Co_{21}Al_2B_6$	”	10 °C/h	”	10.495 (1)		Co_2B
$Co_{20}Al_3B_6$	”	”	”	10.5133 (6)		Co, Co_2B
$Co_{20}Al_3B_{12}$	”	”	”	10.503 (2)		Co_2B, CoB, AlCo
Co/Sn/B						
$Co_{22}SnB_6$	1450 °C/2 h	15 °C/h	1000 °C	10.597 (2)		Co
$Co_{21}Sn_2B_6$	”	”	”	10.594 (6)		$CoSn_2$
$Co_{20}Sn_3B_6$	”	”	”	10.593 (4)	10.5553 (15)	Co_3Sn_2
$Co_{13}Sn_{10}B_6$	”	”	”			$\mathbf{Co_2B}$, Sn, CoSn
$Co_{22}SnB_{12}$	”	”	”			$\mathbf{Co_2B}$, CoSn, Sn
$Co_{20}Sn_3B_{12}$	”	”	”			$\mathbf{Co_2B}$, CoSn
$Co_{10}Sn_{13}B_{12}$	”	”	”			**CoB**, $CoSn_2$
Co/Mg/B	1250 °C/10 h	15 °C/h	800 °C			
$Co_{20}Mg_3B_6$	”	”	”			$\mathbf{Co_2B}$, Co_3B
$Co_{13}Mg_{10}B_6$	”	”	”	10.560 (2)		$\mathbf{Co_2B}$, Co
Co/In/B	1300 °C/1 h	10 °C/h	900 °C			
$Co_{22}InB_6$	”	”	”	10.553 (2)		$\mathbf{Co_4B}$, Co_3B, Co_2B
$Co_{22.3}In_{0.7}B_6$	”	”	”			Co_2B, Co
$Co_{22.4}In_{0.6}B_6$	”	”	”			$\mathbf{Co_3B}$, $\gg Co_{23}B_6$
$Co_{22.5}In_{0.5}B_6$	”	”	”	10.467 (2)	10.4618 (13)	–
$Co_{22.6}In_{0.4}B_6$	”	”	”	10.476 (2)		–
$Co_{23}B_6$	”	”	”			$\mathbf{Co_3B}$, Co
$Co_{22.4}In_{0.6}B_6$	1300 °C/1 h	300 °C/h	25 °C			$\mathbf{Co_3B}$, Co
Co/Ir/B	1450 °C/1 h	10 °C/h	1000 °C			
$Co_{19}Ir_4B_{15}$	”	”	”			Co_2B, CoB, Ir
$Co_{16}Ir_7B_{15}$	”	”	”	10.863 (2)		$IrB_{1.1}$, Ir,
$Co_{13.5}Ir_{9.5}B_{15}$	”	”	”	10.980 (2)	10.9393 (13)	$IrB_{1.1}$
$Co_9Ir_{14}B_{15}$	”	”	”	11.043 (7)		$\mathbf{IrB_{1.1}}$, Ir, $Co_{7-x}Ir_xB_3$
$Co_{15}Ir_8B_6$	1450/10 h	25 °C/h	600 °C	10.840 (8)	10.7979 (16)	
$Co_{20}Ir_3B_6$	”	”	”			$\mathbf{Co_3B}$, Ir

mixed Co/Ga-occupation of site 8c and an occupation by Co of the other sites results in the same ratio Co:Ga as it was obtained by EDX (Co: 95%, Ga: 5%).

$Co_{23}B_6$: The refinement of the single crystal data confirms a binary τ-boride. The lattice parameter of 10.4618(13) Å is the smallest ever found for a τ-boride of cobalt. All metal positions are completely occupied by Co according to the very small standard deviations. A mixed Co/In occupation of the sites 4a and 8c resulted in In-contents less than 1%. This is in agreement with the EDX measurements which detected within the limits ($\approx$1% for heavy atoms) no additional metal except cobalt.

$Co_{16.2}Ir_{6.8}B_6$: The occupation factors of the metal positions showed that Co and Ir are not completely ordered but have different site preferences. The occupation factors for Co1/Ir1, Co2/Ir2 and Co3/Ir3 were combined in a way that full occupation of the sites is achieved. For a stable refinement one of the ratios was fixed and the two other ratios refined as free variables. The fixed ratios were fitted in a way that the overall composition from the refinement corresponds to the Co/Ir ratio found by EDX measurements (Co: 70%, Ir: 30%). The boron site 24e can be derived from difference Fourier synthesis with a value of 8.3 $e^-/Å^3$. All the following maxima of 1.5–2.0 $e^-/Å^3$ are due to the “background” (minimum: $-2.5\,e^-/Å^3$, standard deviation 0.45 $e^-/Å^3$). Finally R-values of $R_1(F) = 0.014$ and $wR_2(F^2) = 0.023$ were received.

$Co_{12.3}Ir_{8.9}B_{10.5}$: The refinement showed the expected mixed Co/Ir occupation of the sites 32f and 48h. The occupation factors were fixed in a way that it fitted the EDX results of 58% Co and 42% Ir. The B1-site was easily localised by difference Fourier syntheses (10.6 $e^-/Å^3$).

Surprisingly the site 8*c* was found to be nearly free (9.5 $e^-/Å^3$, compared to Co4 on site 4*a* with 106 $e^-/Å^3$). Additionally a residual electron density of 5.9 $e^-/Å^3$ occurred on a 32*f* (*x*,*x*,*x*) with $x = 0.197$. Fig. 2 shows the residual electron density obtained by difference Fourier synthesis. For this the refinement was done with partially occupied metal sites and without additional boron (B2). Similar observations were made for $Ni_{20}AlB_{14}$, where the same site is occupied by a B-atom to form a B_4-tetrahedron. Therefore it was assumed that the same is true in this boron-rich τ-boride. The partial occupation reduced the *R*-factors significantly (without B2: $R_1(F) = 0.024$, $wR_2(I) = 0.035$; with B2: $R_1(F) = 0.019$, $wR_2(I) = 0.025$).

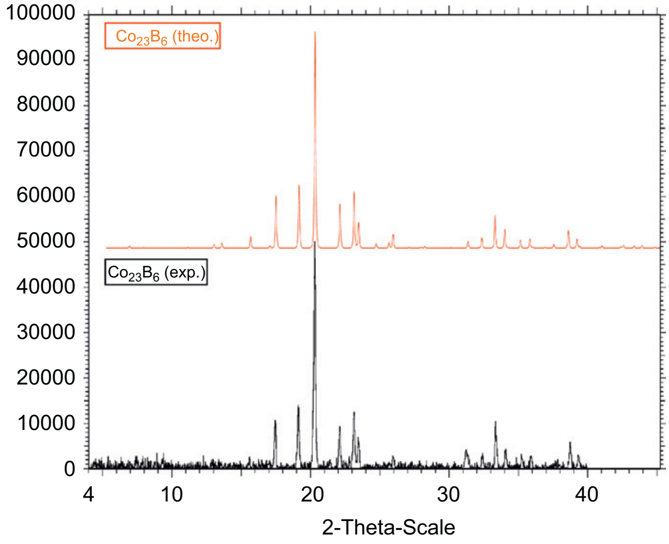

Fig. 1. Experimental (bottom) and calculated (top) X-ray diagram of $Co_{23}B_6$.

3. Results and discussion

The crystal structure of τ-phases was first determined for $Cr_{23}C_6$ [2]. Boron or carbon, respectively, have a quadratic antiprismatic coordination. The same coordination is found for the binary borides of those transition metals (Cr_2B, Mn_2B, Fe_2B, Co_2B, Ni_2B [1]), which are also the most frequent metals for τ-borides. Fig. 3 shows the crystal structure of a τ-phase with a special emphasis on the four different metal positions. It is built up by a cubic face-centred packing of cuboctahedra which are formed by the metal atoms *M*2 on site 48*h* and centred by the metals *M*4 on site 4*a*. The octahedral "voids" are filled by cubes of the metal atoms *M*1 on site 32*f* (*M*1) and the atoms *M*3 on site 8*c* occupy the tetrahedral "voids". The quadratic antiprismatic coordination of the boron atoms is formed by the square planes of the cuboctahedra and the cubes. Coordination polyhedra are shown in Fig. 4.

Table 2
Data for crystal structure analyses of τ-borides Co/*M*′/B (*M*′ = Al, Sn, Ga, Ir), e.s.d.'s in parentheses.

Compound	$Co_{20.9}Al_{2.1}B_6$	$Co_{21.4}Sn_{1.6}B_6$	$Co_{21.9}Ga_{1.1}B_6$	$Co_{23}B_6$	$Co_{16.2}Ir_{6.8}B_6$	$Co_{12.3}Ir_{8.9}B_{10.5}$
Temperature			293 (2) K			
Crystal shape	irregular polyhedron	irregular polyhedron	irregular polyhedron	irregular polyhedron	irregular polyhedron	irregular polyhedron
Size (mm^3)	0.04 × 0.04 × 0.04	0.02 × 0.02 × 0.02	0.04 × 0.04 × 0.04	0.03 × 0.03 × 0.03	0.01 × 0.01 × 0.01	0.01 × 0.01 × 0.01
Crystal system			cubic			
Space group			$Fm\bar{3}m$ (Nr. 225)			
No. of formula units			$Z = 4$			
Unit cell (Å)	$a = 10.4817$ (18)	$a = 10.5553$ (15)	$a = 10.4844$ (15)	$a = 10.4618$ (13)	$A = 10.7979$ (16)	$a = 10.9393$ (13) Å
Volume ($Å^3$)	$V = 1151.6$ (3)	$V = 1176.0$ (3)	$V = 1152.5$ (3)	$V = 1145.2$ (2)	$V = 1259.0$ (3)	$V = 1309.1$ (3) $Å^3$
$d_{calc.}$ (g/cm^3)	7.808	8.548	8.256	8.239	12.285	12.960
Data collection			STOE IPDS II			
Radiation			MoK_α; $\lambda = 0.71073$ Å (graphite monochromated)			
	$0° \leqslant \omega \leqslant 180°$	$0° \leqslant \omega \leqslant 180°$	$0° \leqslant \omega \leqslant 180°$	$0° \leqslant \omega \leqslant 180°$	$0° \leqslant \omega \leqslant 180°$	$0° \leqslant \omega \leqslant 180°$
	$\psi = 0°, 111; \Delta\omega = 2°$	$\psi = 0°, 111; \Delta\omega = 2°$	$\psi = 0°, 111; \Delta\omega = 2°$	$\psi = 0°, 111; \Delta\omega = 2°$	$\psi = 0°, 111; \Delta\omega = 2°$	$\psi = 0°, 111; \Delta\omega = 2°$
Exposure time (s)	300	300	300	300	300	300
Theta range	$6.7° < 2\theta < 67.4°$	$6.7° < 2\theta < 70°$	$6.7° < 2\theta < 70°$	$6.7° < 2\theta < 66°$	$3° < 2\theta < 64°$	$3° < 2\theta < 65°$
	$-16 < h < 16$	$-16 < h < 16$	$-16 < h < 16$	$-16 < h < 16$	$-16 < h < 16$	$-16 < h < 16$
	$-16 < k < 16$	$-16 < k < 16$	$-16 < k < 16$	$-16 < k < 16$	$-16 < k < 16$	$-16 < k < 16$
	$-16 < l < 16$	$-16 < l < 16$	$-16 < l < 16$	$-16 < l < 16$	$-16 < l < 16$	$-16 < l < 16$
μ (mm^{-1})	29.32	32.50	33.04	32.23	92.3	105.4
Absorption correction			numerical/equivalent (XSHAPE [14])			
$R_{int.}/R_{sigma}$	0.117/0.109	0.121/0.051	0.130/0.110	0.053/0.023	0.112/0.079	0.126/0.052
T_{min}/T_{max}	0.200/0.395	0.099/0.392	0.191/0.398	0.282/0.524	0.005/0.043	0.003/0.034
Refinement			SHELXL [13]; full-matrix least squares refinement on F^2			
N(hkl) meas.; unique	6613, 147	8623, 163	8602, 159	6576, 134	6412, 138	6353; 151
N′(hkl) ($I > 2\sigma(I)$)	86	127	98	104	107	125
Parameters refined	15	15	15	14	16	17
R-values $R_1(F)/wR_2(F^2)$	0.0176/0.0192	0.0138/0.0239	0.0272/0.0287	0.0132/0.0210	0.0139/0.0226	0.0189/0.0250
$R_1(F)$, all data	0.0380	0.0235	0.0581	0.0268	0.0227	0.0304
Weighting scheme [13]	0.0/0.0	0.0107/0.0	0.0/0.0	0.0082/0.0	0.0095/0.0	0.0091/0.0
Extinction correction [13]	0.00092 (3)	0.00122 (5)	0.00070 (3)	0.00047 (2)	0.00033 (1)	0.00017 (1)
Goodness of fit	0.449	0.774	0.643	0.830	0.739	0.772
Residual electron density in ($e^-/Å^3$) (max., min., σ)	+0.86/−1.06/0.19	+0.67/−0.76/0.15	+0.88/−0.93/0.35	+0.58/−0.38/0.12	+1.51/−0.87/0.23	+2.09/−1.90/0.34

Table 3
Coordinates, displacements parameters, and occupation factors of τ-borides Co/M'/B (M' = Al, Sn, Ga, Ir).

Compound	$Co_{20.9}Al_{2.1}B_6$	$Co_{21.9}Ga_{1.1}B_6$	$Co_{21.4}Sn_{1.6}B_6$	$Co_{23}B_6$	$Co_{16.2}Ir_{6.8}B_6$	$Co_{12.3}Ir_{8.9}B_{10.5}$
Co1, site 32*f* (*x*,*x*,*x*)						
x	0.38271 (5)	0.38159 (7)	0.38399 (4)	0.38055 (3)	0.37867 (3)	0.37603 (3)
$U_{eq.}$	0.0066 (2)	0.0075 (3)	0.0075 (1)	0.0077 (1)	0.0131 (2)	0.0100 (2)
sof Co/*M*	99.2 (5)[a]	100.4 (5)[a]	100.3 (5)[a]	100.8 (4)[a]	60.2 (3)/39.8[b]	24.0 (5)/76.0[b]
$U_{11} = U_{22} = U_{33}$	0.0066 (2)	0.0075 (3)	0.0075 (1)	0.0077 (1)	0.0128 (2)	0.0100 (2)
$U_{12} = U_{13} = U_{23}$	0.0003 (2)	0.0004 (3)	0.0020 (1)	0.0012 (1)	0.0018 (2)	0.0010 (1)
Co2, site 48*h* (0,*y*,*y*)						
y	0.16980 (5)	0.16912 (6)	0.16886 (4)	0.16948 (3)	0.16821 (4)	0.16603 (5)
$U_{eq.}$	0.0074 (2)	0.0074 (2)	0.0065 (1)	0.0077 (1)	0.0132 (2)	0.0080 (2)
sof Co/*M*	101.0 (5)[a]	99.1 (6)[a]	99.8 (6)	99.2 (5)a	72.6 (3)/27.4[b]	76.0 (8)/23.2[b]
U_{11}	0.0091 (4)	0.0091 (4)	0.0072 (2)	0.0092 (1)	0.0146 (3)	0.0081 (3)
$U_{22} = U_{33}$	0.0065 (2)	0.0065 (3)	0.0061 (2)	0.0070 (1)	0.0126 (2)	0.0080 (2)
U_{23}	0.0005 (3)	−0.0001 (3)	0.0002 (2)	0.0004 (1)	0.0001 (2)	0.0000 (2)
Co3, site 8*c* ($\frac{1}{4},\frac{1}{4},\frac{1}{4}$)						
U_{iso}	0.0085 (13)	0.0098 (7)	0.0079 (2)	0.0088 (2)	0.0155 (7)	0.0060 (14)[c]
sof Co/*M*	4.8 (17)/95.2[b]	44.5 (13)/56.5[b]	22.1 (6)/77.9[b]	98.9 (9)[a]	83.6 (5)/16.4[b]	3.3 (4)
Co4, site 4*a* (0,0,0)						
U_{iso}	0.0089 (12)	0.0071 (8)	0.0074 (4)	0.0083 (3)	0.0097 (7)	0.0060 (14)[c]
sof Co/*M*	82 (4)/18[b]	101 (2)[a]	96.6 (2)	100.7 (14)[a]	107 (2)[a]	93.4 (17)/6.6[b]
B1, site 24*e* (0,0,*z*)						
z	0.2743 (9)	0.2736 (12)	0.2757 (6)	0.2756 (5)	0.2765 (11)	0.2745 (16)
$U_{eq.}$	0.0049 (13)	0.0063 (17)	0.0093 (10)	0.0081 (8)	0.0134 (20)	0.013 (2)[d]
sof	96 (2)[a]	104 (3)[a]	96 (5)[a]	98 (3)[a]	91 (7)[a]	95 (5)[a]
$U_{11} = U_{22}$	–	0.005 (2)	0.0121 (15)	0.0085 (13)	0.0157 (29)	–
U_{33}	–	0.009 (5)	0.004 (2)	0.007 (2)	0.009 (5)	–
B2, site 32*f* (*x*,*x*,*x*)						
x						0.1974 (13)
$U_{eq.}$						0.013 (2)[d]
Sof						57 (6)

[a] 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 discussion a full occupation is assumed.

[b] Refined as mixed occupation Co/*M* (M = Al, Ga, Ir), in sum a full occupation is assumed.

[c,d] Coupled refinement.

3.1. $Co_{23-x}Mg_xB_6$, $Co_{23-x}Al_xB_6$, $Co_{23-x}Ga_xB_6$, $Co_{23-x}Sn_xB_6$ ($1<x<3$)

Because of its interesting mechanical and magnetic properties [3,15–17], the phase equilibria of the ternary systems Co/M'/B (M' = Mg, Al, Ga, Sn) were already investigated by sintering techniques (i.e., melting and subsequent annealing). Samples were characterised by X-ray powder methods and metallographic investigations. Our findings confirm the earlier results.

For M' = Mg no single crystals were obtained but the existence of boron-rich and/or Mg-rich τ-phases is very unlikely. The lattice constant of 10.560(2) Å is in good agreement with a value of 10.541 Å published by Stadelmaier [3] for $Co_{23-x}Mg_xB_6$. For the analogous Ni-containing τ-boride $Ni_{20}Mg_3B_6$ a value of 10.567 Å is given [3,17]. Because the metallic radius of Mg (1.60 Å) is comparable to Sn (1.58 Å) compositions between $Co_{21}Mg_2B_6$ and $Co_{22}MgB_6$ are expected.

The results of the single crystal data refinement are similar for M' = Al, Ga, and Sn. According to the variation of the lattice parameter of the powder samples there is no boron-rich τ-phase, in contrast to the analogous Ni-compounds [6,7]. Furthermore the sites 48*h* and 32*f* cannot be substituted by M' and 8*c* is the preferred site for M'. For M' = Al a nearly complete occupation by Al is possible and, additionally, a part of the 4*a* site. The variation of the lattice parameter with different M' corresponds to the values of the atomic radii (Al = 1.43 Å, Ga = 1.39 Å, Sn = 1.58 Å) and the content of M'. The distances Co–M3/Co3 (Table 4) reflect the same relations and are not discussed in detail.

Our results for the system with M' = Al confirm and state more precisely the data given in the literature. Stadelmaier et al. [19] and Kuz'ma et al. [20] reported on a τ-boride with compositions between $Co_{20}Al_3B_6$ (a = 10.52 Å) and $Co_{20.4}Al_{2.6}B_6$ (a = 10.48 Å). They assumed an ideal composition of $Co_{20}Al_3B_6$. The τ-boride is in equilibrium with Co_2B and AlCo. According to our investigations additional boron is not taken up by the τ-phase but results in formation of Co_2B and CoB. Variation of the Al-ratio gives no access to $Co_{23}B_6$. According to the single crystal data both sites 4*a* and 8*c* are involved in the substitution, but 8*c* is clearly preferred.

τ-borides $Co_{23-x}Ga_xB_6$ were already known. According to microprobe measurements Fiedler et al. [21] gave the composition $Co_{21}Ga_2B_6$ and a = 10.519 Å. Kuz'ma [22] and Buschow [15] communicated the composition $Co_{20}Ga_3B_6$ and lattice parameters of 10.51 Å and 10.52 Å, respectively. Our results confirm these findings in general. Because Co and Ga have similar electron numbers the localisation of Ga is less reliable. But obviously the substitution occurs mainly an site 8*c*. It is to mention that $Co_{23}B_6$ was not observed with M' = Ga.

In $Co_{23-x}Sn_xB_6$ the range of homogeneity is quite small and there is no boron-rich τ-phase. This confirms the results of Stadelmayer et al. [2,23] who gave 10.60 Å and the composition $Co_{21}Sn_2B_6$. The size of Sn results in an enlargement of the lattice

Table 4
Selected distances in τ-borides Co/*M*/B (*M* = Al, Ga, Sn, Ir), e.s.d.'s in parentheses.

Compound	$Co_{20.9}Al_{2.1}B_6$	$Co_{21.9}Ga_{1.1}B_6$	$Co_{21.4}Sn_{1.6}B_6$	$Co_{23}B_6$	$Co_{16.2}Ir_{6.8}B_6$	$Co_{12.3}Ir_{8.9}B_{10.5}$
Co1–B1 3*x*	2.077 (5)	2.090 (7)	2.075 (4)	2.081 (3)	2.157 (6)	2.216 (9)
*M*3	2.4099 (9)	2.3898 (13)	2.4496 (8)	2.3657 (6)	2.4064 (7)	2.3879 (6)
*M*1 3*x*	2.4595 (10)	2.4827 (15)	2.4491 (9)	2.4993 (7)	2.6203 (8)	2.7123 (7)
*M*2 6*x*	2.6073 (6)	2.6050 (7)	2.6395 (5)	2.5907 (4)	2.6714 (5)	2.7071 (5)
B2 3*x*						2.260 (2)
Co2–B1 2*x*	2.090 (5)	2.083 (7)	2.109 (4)	2.092 (3)	2.160 (7)	2.170 (9)
*M*2	2.3784 (15)	2.3982 (19)	2.4224 (11)	2.3826 (9)	2.4975 (11)	2.5982 (10)
*M*2 4*x*	2.5176 (8)	2.5077 (10)	2.5207 (6)	2.5075 (5)	2.5689 (7)	2.5685 (8)
*M*4	2.5176 (8)	2.5077 (10)	2.5207 (6)	2.5075 (5)	2.5689 (7)	2.5685 (8)
*M*1 4*x*	2.6073 (6)	2.6050 (7)	2.6395 (6)	2.5907 (4)	2.6714 (5)	2.7071 (5)
*M*3 2*x*	2.8783 (6)	2.8824 (6)	2.9305 (5)	2.8740 (4)	2.9743 (5)	3.0282 (5)
B2 2*x*						2.215 (18)
Co3–*M*1 4*x*	2.4099 (9)	2.3898 (13)	2.4496 (8)	2.3657 (6)	2.4064 (7)	2.3879 (6)
*M*2 12*x*	2.8783 (6)	2.8824 (6)	2.9305 (5)	2.8740 (4)	2.9743 (5)	3.0282 (5)
B2 4*x*						0.994 (25)
Co4–*M*2 12*x*	2.5176 (8)	2.5077 (10)	2.5207 (6)	2.5075 (5)	2.5689 (7)	2.5685 (8)
B1–*M*1 4*x*	2.077 (5)	2.090 (7)	2.075 (4)	2.081 (3)	2.157 (6)	2.216 (9)
*M*2 4*x*	2.090 (5)	2.083 (7)	2.109 (4)	2.092 (3)	2.160 (7)	2.170 (9)
B2–Co3						0.996 (25)
B2 3*x*						1.63 (4)
*M*2 3*x*						2.214 (18)
*M*1 3*x*						2.260 (2)

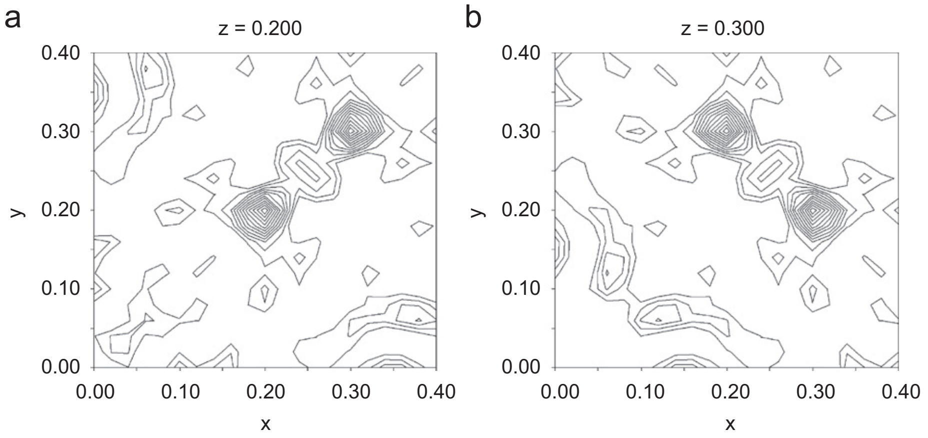

Fig. 2. Difference Fourier maps at $z = 0.20$ and $z = 0.30$ of $Co_{12.3}Ir_{8.9}B_{10.5}$ without the additional site B2.

parameter. We obtained values of about 10.59 Å from powder samples and of 10.56 Å from single crystals. According to the single crystal data refinement the Sn-substitution is limited to the *M*3 site. Therefore the distances around *M*3 are significantly longer compared to $Co_{23}B_6$ while the others are quite similar.

3.2. Co/In/B; $Co_{23}B_6$

The system Co/In/B is more complex. In agreement to the published data [24,25] In-containing τ-phases $Co_{23-x}In_xB_6$ are stable for $x \approx 1$. With respect to the radius of In the lattice parameter of $a = 10.551$ Å is consistent with this composition. EDX measurements of a fragment of the crushed melt revealed an In-content of 3 at%. With lower In-content a τ-boride resulted with a very small lattice parameter of 10.465–10.475 Å. According to EDX and X-ray investigations it is a binary $Co_{23}B_6$. Single crystals of the In-containing τ-phase (i.e., $a = 10.55$ Å) which were suitable for an X-ray investigation could not be isolated from the melt. Because the powder pattern of samples with compositions between $Co_{22.5}In_{0.5}B_6$ and $Co_{22.6}In_{0.4}B_6$ showed only reflections of $Co_{23}B_6$ we assume the decomposition of these τ-phases to $Co_{23}B_6$ and In. Nevertheless small amounts of In are essential for the formation of $Co_{23}B_6$ because samples free from indium never yielded a τ-phase, which is in accordance to the phase investigations by Ganglberger et al. [26]. The formation of $Co_{23}B_6$ single crystals under the influence of indium is also in accordance with the observation that fast cooling (300 °C/h) disables the formation of a τ-boride.

In connection to the formation of glasses (see below) the role of In can also seen as a flux for the origination of $Co_{23}B_6$ and its crystallisation. The liquid system Co/In shows a miscability gap

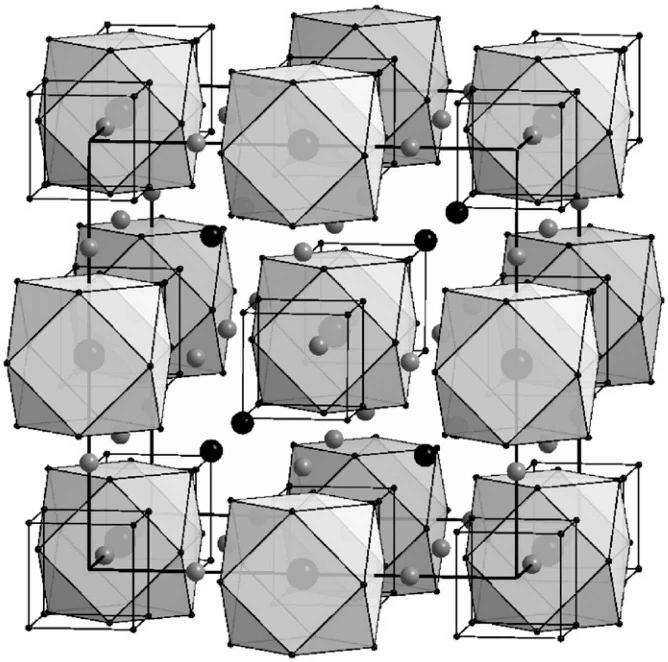

Fig. 3. Crystal structure of τ-Borides $M_{23}B_6$; $M1$: M_8-cubes, $M2$: M_{12}-cuboctahedra centred by $M3$, isolated M-atoms: $M4$; grey circles: boron, black circles: metal atoms.

over the whole range of the melt [27] which may favour the formation of a binary $Co_{23}B_6$. Still it is not clear whether $Co_{23}B_6$ is a metastable phase or exists in the sub-solidus field as a stable phase.

The crystal structure of $Co_{23}B_6$ is in a line with the other Co-containing τ-borides ($M' =$ Al, Ga, Sn). The small lattice parameter results from the metallic radius of Co. The short distances Co1–Co3 (2.366 Å) clearly indicate the occupation of 8*c* by Co. The other distances are very similar to $Co_{20.9}Al_{2.1}B_6$ and $Co_{21.9}Ga_{1.1}B_6$. The Co–B-distances of 2.081 and 2.092 Å are comparable to other binary Co-borides (for example Co_2B: Co–B: 2.144 Å, Co–Co: 2.383 Å [28]). $Co_{23}B_6$ shows the smallest lattice parameter ever found for a τ-phase with Co.

The existence of binary τ-borides is in discussion because of several reasons. It is well-known that alloys of late transition metals $TM_{80}B_{20}$ ($TM =$ Fe, Co, Ni) have a tendency to form glasses [29]. Therefore there are several reports on binary τ-phases but a definite characterisation is still missing.

A detailed investigation of the Co/B-system was given by Schöbel and Stadelmaier [30]. They reported three stable binary borides. Co_2B and CoB melt congruently at 1280 and 1460 °C, respectively. Peritectic Co_3B (cementite-type) is stable up to 1125 °C, quite close to the eutectic point (1110 °C, 18.4 at% B). A τ-phase was not observed. Bashev et al. [31] investigated metastable phases by melt-spinning (cooling rate 10^6 °/sec) and obtained the τ-phases $Fe_{23}B_6$ (10.69 Å) and $Co_{23}B_6$ (11.05 Å). While the value for $Fe_{23}B_6$ can be estimated from ternary τ-borides of Fe the value for $Co_{23}B_6$ is not plausible. The existence of metastable $Fe_{23}B_6$ (10.69 Å) in splat-cooled samples was confirmed by Herold and Köster [32]. Later on its formation from amorphous $Fe_{84}B_{16}$ was observed between 925 and 1075 K (10.76 Å), but not as a single phase [33]. Recently [34] $Ni_{23}B_6$ was described as a metastable phase within the system Ni/B which is formed around 1000 °C from undercooled Ni–B-alloys. $Ni_{23}B_6$ was identified by XRD but no details (lattice parameter, intensities) are given. So to our knowledge there was no well characterised binary τ-boride up to now and this is the first characterisation of a single crystal of a τ-boride. Furthermore $Co_{23}B_6$ represents the only binary τ-phase besides the carbides $Cr_{23}C_6$ [35] and $Mn_{23}C_6$ [36].

3.3. τ-Phases Co/Ir/B

3.3.1. $Co_{16.2}Ir_{6.8}B_6$

Iridium plays a special role as a τ-stabilizer because the degree of substitution exceeds the usual value of $x = 3$ considerably and τ-phases with $1 > x > 3$ could not be synthesised. Similar observations were already made for the τ-borides with Cr [8,37], Mn [4], Fe [4,37] and Ni [6,37]. An Ir-rich τ-boride $Co_{15}Ir_8B_{6+x}$ with $a = 10.855$ Å was already described by Rogl and Nowotny [4]. In contrast to the analogous Fe-compounds, no assignment of Ir to preferred sites was done. The single crystal data revealed the partial occupation of the sites 48*h* ($M2$) and 32*f* ($M1$) by Ir. The preference of the $M1$-site by Ir was already observed for $Cr_{7.9}Ir_{14.1}B_6$ [8]. The distances in $Co_{17.2}Ir_{5.8}B_6$ reflect the substitution of Co by Ir on the sites $M1$ and $M2$. Because of greater metallic radius of Ir (1.35 Å) compared to Co (1.26 Å) the distances $M1$–$M1$, $M1$–$M2$ and $M2$–$M2$ are significantly enlarged. The same is found for the distances M–B. The different metallic radii have an impact also on the lattice parameter. The value for a hypothetic $Ir_{23}B_6$ can be estimated from the series $Cr_{23-x}Ir_xB_6$ [8] and $Fe_{23-x}Ir_xB_6$ ($7 \leqslant x \leqslant 16$) investigated by Rogl et al. [4] and Ade et al. [37] to a value of $a = 11.50$ Å to $a = 11.60$ Å. According to the ratio Co:Ir in $Co_{16.2}Ir_{6.8}B_6$ a lattice parameter between 10.75 Å and 10.80 Å is expected, which agrees well to the experiment.

3.3.2. $Co_{12.3}Ir_{8.9}B_{10.5}$

The possibility of an enlarged boron-content was already discussed by Rogl and Nowotny [4]. Stadelmaier proposed for boron-rich τ-borides $Ni_{20}Al_3B_{6+x}$ [18,19] the substitution of isolated B-atoms by B_2-units. Although this mechanism was questioned by geometrical considerations no alternative proposals were given.

According to the single crystal results the rise of the boron content results from the substitution of $M3$ by B_4-tetrahedra. The enlargement of the lattice parameter results from the Co-Ir substitution and the B_4-tetrahedra as well. The effects of the first was already seen and discussed for $Co_{16.2}Ir_{6.8}B_6$. The influence of the latter is smaller and can be estimated from the system Ni/Al/B ($Ni_{20}Al_3B_6$: $a = 10.511$ Å, $Ni_{20}AlB_{14}$: $a = 10.617$ Å). The observed lattice parameter for the single crystal $Co_{12.3}Ir_{8.9}B_{10.5}$ (10.939 Å) agrees well to the value expected for this composition. The highest value observed for the powder samples (11.05 Å) corresponds to an Ir/Co-substitution of about 50%.

All structural features from the refinement of the single crystal data are in accord with these two patterns of substitution. According to the atomic radii the substitution of Co by Ir results in an enlargement of most of the M–M-distances. This is the more pronounced the higher the Ir-content is. So the distance $M1$–B1 ($M1$ with 76% Ir) rises from 2.16 to 2.22 Å while $M2$–B1 ($M2$ with 23% Ir) remains nearly unchanged (2.16/2.17 Å) similar to the distances $M2$–$M4$. A marked difference is observed for the distance $M1$–$M3$, which is 2.406 Å in $Co_{16.2}Ir_{6.8}B_6$ and 2.388 Å in the boron-rich phase, where the $M3$ site is nearly empty. The additional site of B2 performs a perfect surrounding for boron and a B_4-tetrahedron, respectively (Fig. 4). The distances $M1$–B2 (2.26 Å) and $M2$–B2 (2.21 Å) are comparable to the distances of B1. B–B-distances of 1.63(4) Å within the B_4-tetrahedron are the values expected ($Ni_{20}AlB_{14}$: 1.681(15) Å, B_4Cl_4: 1.68–1.69 Å [38], 1.65 Å [39]; $(tBu)_4B_4$: 1.71 Å [40]).

Despite the excellent *R*-values of the refinement, the interpretation of the results contains still some uncertainties. Because of the high electron number of iridium the standard deviation of

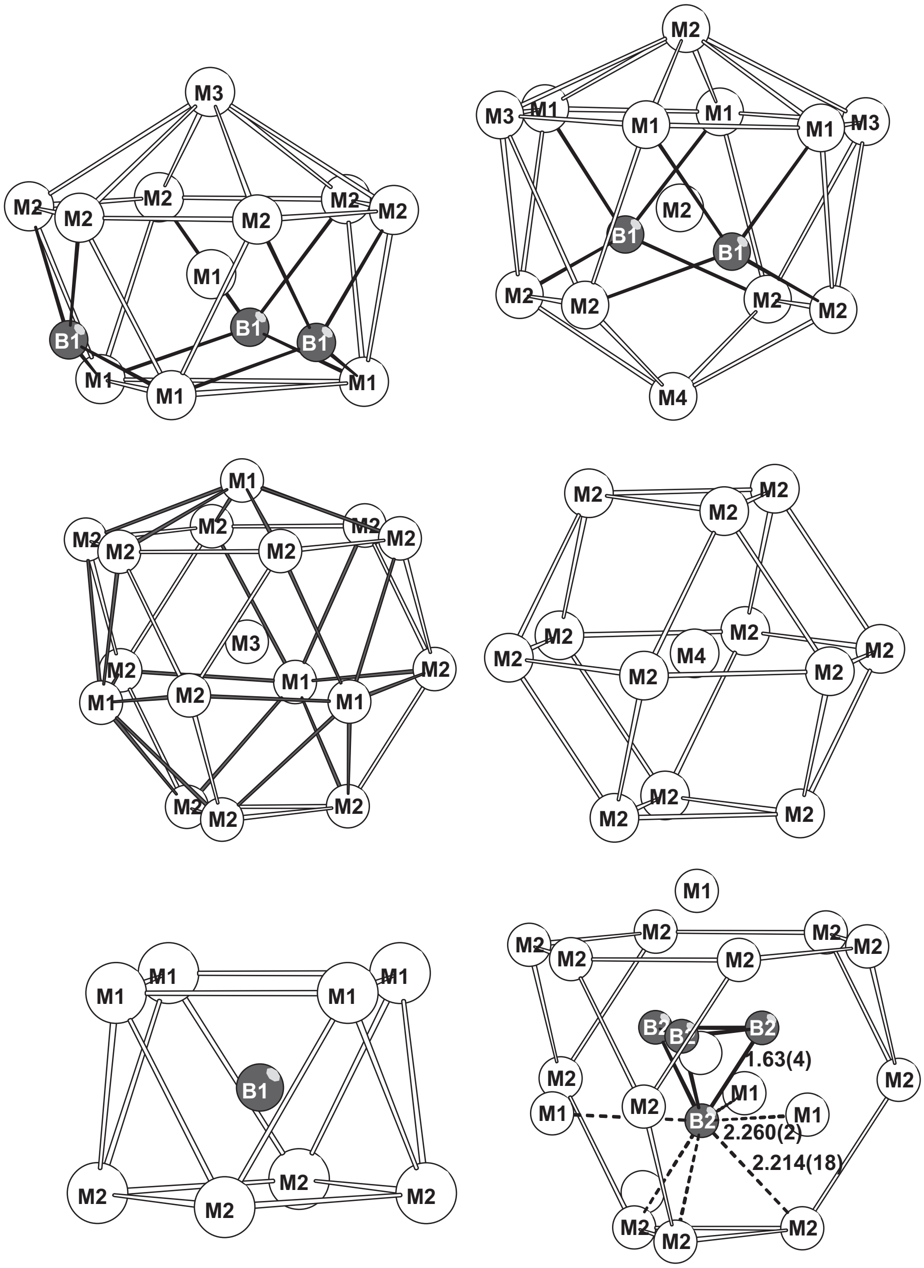

Fig. 4. Coordination polyhedra in τ-borides (B_4-tetrahedron for $Co_{12.3}Ir_{8.9}B_{10.5}$).

the site occupation factor of B2 is quite large. A reliable quantitative determination of the boron content was impossible because of experimental problems (s. above). Nevertheless several reasons favour the substitution $M3 \leftrightarrow B_4$. Similar to $Ni_{20}AlB_{14}$ site 8*c* is clearly almost unoccupied and there is a residual electron density on site 32*f* (x, x, x) with $x = 0.194$. Both observations are coupled to the enlarged boron content. The occupation factors of *M*3 and B2 have not necessarily to sum up to 1/24. It is known from other τ-borides that the 8*c* site can show an incomplete occupation [8]. The samples with the compositions $Co_{13.5}Ir_{9.5}B_{15}$ and $Co_{16}Ir_7B_{15}$ contain only very small amounts of $IrB_{1.1}$ and no further borides. There are no hints for unreacted boron or the formation of volatile boron oxides (no loss of weight). Therefore most of the boron must have been transferred to the τ-boride. The coordination of B2 is a threefold capped trigonal prism. This coordination is by far the most common for binary and ternary borides of transition metals. Usually the trigonal prism is formed by metal atoms and the rectangular sites are capped by metal or boron, depending from the ratio metal:boron. With a composition M_3B (for example Co_3B–cementite-type [1]) all sides are capped by metal atoms, in monoborides (CoB [1]) two are capped by boron forming zick–zack chains, and in diborides MB_2 (i.e., CrB_2 [1]) all sides are capped by boron. With intermediate compositions the different types are combined (Cr_2IrB_2: 1 and 2 sides are capped [8]). So the existence of B_4-tetrahedra in $Co_{12.3}Ir_{8.9}B_{10.5}$ is very likely, but B_3-triangles or B_2-dumbbells cannot totally be excluded.

A high Ir-content, i.e., $x > 3$ and Ir on the sites 32*f* and 48*h*, is a condition for the existence of a τ-phase. Similar observations were made for τ-borides $Cr_{23-x}Ir_xB_6$, but here no boron-rich phase was found [8]. In order to check for the influence of the atomic size we investigated the τ-borides of the systems Co/Ti/B and Co/V/B, where M' has a similar size ($r_{Ti} = 1.45$ Å, $r_V = 1.36$ Å). Both τ-borides were already described earlier. On the basis of powder data different compositions and lattice parameters were communicated ($Co_{20}Ti_3B_6$: $a = 10.549$ Å [15], $a = 10.526$ Å [41], $a = 10.577$ Å [26]; $Co_{21}Ti_2B_6$: $a = 10.510$ Å [42]); $Co_{20}V_3B_6$: $a = 10.489$ Å [43], $a = 10.497$ Å [44]; $Co_{21}V_2B_6$: $a = 10.486$ Å [15], $a = 10.479$ Å [42], $a = 10.486$ Å [26]). Our results confirm the very narrow range of homogeneity ($x \approx 2$). Boron-rich phases were not obtained but single crystals for both cases. The refinements showed that Ti and V were mainly localised on site 8*c*, very close to a complete occupation [45] so that resulting compositions are $Co_{21}Ti_2B_6$ and $Co_{21}V_2B_6$. The special situation in Ir-based τ-phases is not a consequence of the atom size but seems to have electronic reasons.

4. Conclusions

The cubic τ-borides $Co_{23-x}M'_xB_6$ with $M' =$ Mg, Al, Ga, In, Sn, Ir, Ti, V were synthesised from the element. On the basis of single crystal data (except Mg and In) and EDX results detailed statements on the arrangement of M' are possible. The crystal structure exhibits four crystallographically different sites so the formula can be written as $M_{12}M_8MM_2B_6$.

If M' is a main group metal the integration of M' takes place preferably on site 8*c*. So they can be described by the formula: $Co_{12}Co_8CoCo_{2-x}M'_xB_6$. Its extent depends on the metals involved. For Ga, Sn and V (and probably Mg and In, too) x is between 0 and 1. For $M' =$ Al and Ti there is an additional participation of the site 4*a* ($Co_{12}Co_8Co_{1-y}M'Co_{2-x}M'_xB_6$). Surprisingly, in contrast to the analogous τ-borides of Ni no boron-rich τ-phases were found.

A special situation is present with $M' =$ In. Obviously caused by a miscibility gap of the metallic melt besides $Co_{22.5}In_{0.5}B_6$ ($a = 10.551$ Å) also the binary $Co_{23}B_6$ ($a = 10.462$ Å) was obtained. $Co_{23}B_6$ is the first example for a well-characterised binary τ-boride.

Iridium as a τ-stabilizer plays a special role. The synthesis of τ-phase $Co_{20+x}Ir_{3-x}B_6$ was impossible and there exist only τ-phases with significantly higher amounts of Ir. Detailed investigations were done for a single crystal with a composition $Co_{17.2}Ir_{5.8}B_6$. The uptake of Ir occurs especially on site 32*f*. Furthermore a boron-rich τ-boride with the composition $Co_{12.3}Ir_{8.9}B_{10.5}$ was characterised. The enlargement of the boron content results from the substitution of metal atoms ($M'3$ on site 8*c*) by B_4-tetrahedra. According to the results of the refinement the site 8*c* is free and to 60% replaced by B_4-tetrahedra. The coordination of this site fits perfectly to the geometrical requirements of a B_4-tetrahedron. This type of substitution was already observed in $Ni_{20}AlB_{14}$, i.e., $Ni_{20}Al(Al)_{2-y}B_6(B_4)_y$ where y represents the substitution of metal atoms by B_4-tetrahedra. $Co_{12.3}Ir_{8.9}B_{10.5}$ is the first example of a boron-rich τ-boride with B_4-tetrahedra, where the transition metal is cobalt. The comparison to $Co_{21}Ti_2B_6$ and $Co_{21}V_2B_6$ shows that the special relations in the system Co/Ir/B is not caused by size effects of the τ-stabiliser M'.

Note in addition

During the review of this contribution we obtained a τ-phase with a composition $Co_{20}Ir_3B_6$ (single crystal: $a = 10.608(1)$ Å, powder: $a = 10.612(2)$ Å). The refinement of the single crystal data revealed a distribution of Ir over all four metal sites with a preference of site 8*c* and avoiding of site 4*a* (135 refl. $83 > 2\sigma(I)$, $R_1(F) = 0.019$, $wR_2(I) = 0.025$) [46].

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[45] $Co_{20.7}Ti_{2.3}B_6$: $a = 10.516(3)$ Å, 109 refl.($100 > 2\sigma(I)$), $R_1(F) = 0.017$, $wR_2(I) = 0.033$, Co1: $x = 0.38276(5)$, $U_{eq.} = 0.0094(2)$; Co2: $y = 0.17022(4)$, $U_{eq.}$ 0.0092(2), Ti3: $U_{eq.} = 0.0079(5)$, Ti4/Co4: 71(6)% Ti, $U_{eq.} = 0.0096(9)$, B: $z = 0.2730(9)$, $U_{eq.}$ 0.0117(15), CSD 419738; $Co_{21.4}V_{1.6}B_6$: $a = 10.4756(12)$ Å, 108 refl.($68 > 2\sigma(I)$), $R_1(F) = 0.026$, $wR_2(I) = 0.053$, Co1: $x = 0.38081(9)$, $U_{eq.} = 0.0171(4)$; Co2: $y = 0.17014(8)$, $U_{eq.}$ 0.0189(4), V3/Co3: 80(7)% V, $U_{eq.} = 0.0162(12)$, Co4: $U_{eq.} = 0.0202(12)$, B: $z = 0.2689(14)$, $U_{iso.}$ 0.0061 (22), CSD 419737.
[46] Synthesis at 1450 K from the elements, composition of the single crystal by EDX: $Co_{20}Ir_3B_6$, refinements were performed with the assumption of mixed occupations yielding similar displacement parameters for all metal atoms; Co-content: *M*1: 89%, *M*2: 88%, *M*3: 98%, *M*4: 65%; further details: CSD 420035.