



Synthesis, crystal structure investigation and magnetism of the complex metal-rich boride series $\text{Cr}_x(\text{Rh}_{1-y}\text{Ru}_y)_{7-x}\text{B}_3$ ($x=0.88-1$; $y=0-1$) with Th_7Fe_3 -type structure

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ABSTRACT

Powder samples and single crystals of the new complex boride series $\text{Cr}_x(\text{Rh}_{1-y}\text{Ru}_y)_{7-x}\text{B}_3$ ($x=0.88-1$; $y=0-1$) have been synthesized by arc-melting the elements under purified argon atmosphere on a water-cooled copper crucible. The products, which have metallic luster, were structurally characterized by single-crystal and powder X-ray diffraction as well as EDX measurements. Within the whole solid solution range the hexagonal Th_7Fe_3 structure type (space group $P6_3mc$, no. 186, $Z=2$) was identified. Single-crystal structure refinement results indicate the presence of chromium at two sites (6c and 2b) of the available three metal Wyckoff sites, with a pronounced preference for the 6c site. An unexpected Rh/Ru site preference was found in the Ru-rich region only, leading to two different magnetic behaviors in the solid solution: The Rh-rich region shows a temperature-independent (Pauli) paramagnetism whereas an additional temperature-dependent paramagnetic component is found in the Ru-rich region.

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1. Introduction

The crystal chemistry and magnetism of metal-rich borides have been intensely studied in recent years [1]. The targeted phases comprise those crystallizing with the Th_7Fe_3 structure type [2] whose general formula $M_xT_{7-x}\text{B}_3$ ($M=\text{Cr, Mn, Fe, Co, Ni}$; $T=\text{Ru, Rh}$) [3–7] implies a substitution of a 4d transition metal T by a 3d element M in the binary phase $T_7\text{B}_3$. These studies have led recently to the first itinerant ferromagnetic borides of this structure type, FeRh_6B_3 and CoRh_6B_3 , with ordering temperatures of 240 and 150 K, respectively [6]. Pauli paramagnetism has been observed in $M_{0.5}\text{Ru}_{6.5}\text{B}_3$ ($M=\text{Cr, Mn, Co, Ni}$) [5] and $M_x\text{Rh}_{7-x}\text{B}_3$ ($M=\text{Cr, Ni}$) [7] and an additional temperature-dependent behavior was observed in NiRh_6B_3 and $\text{Mn}_{0.5}\text{Ru}_{6.5}\text{B}_3$ at low temperatures. The crystal structures of these phases have revealed a strong M/T site preference. For phases with $T=\text{Rh}$ and $x \leq 1$, M substitutes Rh (in the binary Rh_7B_3) at only one (6c) of the available three Wyckoff sites (6c, 6c and 2b) whereas for $x > 1$, two sites are concerned by the substitution. Moving on to phases with $T=\text{Ru}$, two sites are concerned by the substitution already at $x < 1$. A clear trend therefore appears: for $x \leq 1$, rhodium-rich phases tend to accommodate M on only one Wyckoff site whereas those rich in ruthenium prefer M on two sites. Which of the two alternatives will be adopted in a phase with $x \leq 1$ and containing

both rhodium and ruthenium? Until now no phase has been reported containing both elements in this structure type. The presence of both elements in a series of compounds would allow for a study of the evolution of these two different site preferential behaviors. For this purpose, we have carried out synthetic and structural investigations of the “ $\text{CrRh}_{6-n}\text{Ru}_n\text{B}_3$ ($1 \leq n \leq 6$)” series, which is a really complex system because of the possibility to have three elements in one or two different crystallographic sites. Furthermore, the presence of two elements (Ru and Rh) which are not distinguishable by X-ray diffraction methods implies the use of a combination of different analytical methods for a comprehensive understanding of the system. At last, the magnetic properties of the synthesized compounds have been investigated.

2. Results and discussion

2.1. Phase analysis

The synthesized samples were firstly analyzed by X-ray powder diffraction to determine the phases present and refine the lattice parameters. The phase analysis confirmed the expected Th_7Fe_3 structure type for all loaded compositions and isotypism with the recently published $\text{Cr}_x\text{Rh}_{7-x}\text{B}_3$ ($x=0.78$) phase [7]. However, all products were slightly contaminated by a side phase which was identified to be the intermetallic solid solution $(\text{Rh/Ru})_{1-x}\text{Cr}_x$ ($x=0.5$) in the quaternary phases and ruthenium metal in the ternary rhodium-free phase (see Table 1). The side

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Table 1
Results of the Rietveld refinement for the borides with the ideal loaded composition $\text{CrRh}_{6-n}\text{Ru}_n\text{B}_3$ ($1 \leq n \leq 6$).

Loaded composition	$\text{CrRh}_5\text{RuB}_3$	$\text{CrRh}_4\text{Ru}_2\text{B}_3$	$\text{CrRh}_3\text{Ru}_3\text{B}_3$	$\text{CrRh}_2\text{Ru}_4\text{B}_3$	$\text{CrRhRu}_5\text{B}_3$	CrRu_6B_3
Structure refinement	Rietveld, least-squares method					
Cell parameters						
a (Å)	7.427(1)	7.423(1)	7.420(1)	7.416(1)	7.416(1)	7.411(1)
c (Å)	4.742(1)	4.733(1)	4.724(1)	4.712(1)	4.703(1)	4.693(1)
V (Å ³)	226.54(4)	225.86(4)	225.23(3)	224.43(2)	223.98(2)	223.20(2)
Space group; Z	$P6_3mc$ (no. 186); 2					
R_{wp} ; R_{Bragg} ; χ^2	0.06; 0.14; 0.06					
Phase amount (%) side-phase	~99 (Rh/Ru) _{1-x} Cr _x					
	~99 (Rh/Ru) _{1-x} Cr _x	~96 (Rh/Ru) _{1-x} Cr _x	~95 (Rh/Ru) _{1-x} Cr _x	~97 (Rh/Ru) _{1-x} Cr _x	~97 (Rh/Ru) _{1-x} Cr _x	~85Ru

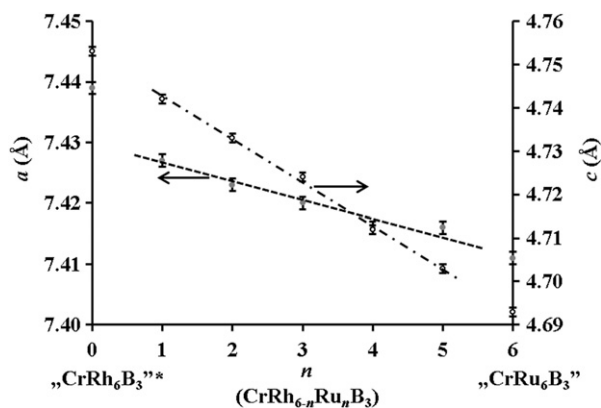


Fig. 1. Lattice parameters (a and c) as a function of the ruthenium content (n) in the ideal loaded composition " $\text{CrRh}_{6-n}\text{Ru}_n\text{B}_3$ ($0 \leq n \leq 6$)". The dotted line represents the linear relationship of the Vegard's law. * result from Ref. [7].

phase $\text{Rh}_{0.75}\text{Cr}_{0.25}\text{B}_3$ was reported in the synthesis of the $\text{Cr}_x\text{Rh}_{7-x}\text{B}_3$ ($x=0.78$) phase. The amount of the main phase obtained from Rietveld refinement lies above 95% in all cases except for the " CrRu_6B_3 " case (85%). The refined lattice parameters (a and c) of the whole series are given in Table 1 and plotted in Fig. 1 as function of the ruthenium content (n) in the ideal loaded composition " $\text{CrRh}_{6-n}\text{Ru}_n\text{B}_3$ ($0 \leq n \leq 6$)". The lattice parameters of all phases are smaller than those reported for the binary phase Rh_7B_3 ($a=7.47$ Å, $c=4.78$ Å, $V=230.9$ Å³) [8], as expected when an element (in our case Cr) with a smaller atomic radius (one half of the bond in the element) substitutes a larger one (Rh). Furthermore, both lattice parameters decrease nearly linearly with increasing ruthenium content (n). The decrease of a and c with increasing n was expected, because the slightly smaller ruthenium increasingly substitutes rhodium in the " $\text{CrRh}_{6-n}\text{Ru}_n\text{B}_3$ ($0 \leq n \leq 6$)" series. The consequence is of course the decrease of the unit cell volume with increasing ruthenium content (see Fig. 2). A Vegard-like behavior is found for nearly all members of the series, a deviation being observed for the Ru-free $\text{Cr}_x\text{Rh}_{7-x}\text{B}_3$ ($x=0.78$) phase. This was, however, expected because in this phase a lower chromium content ($x=0.78$) than expected ($x=1$) was reported, and thus induces larger lattice parameters (see Fig. 1).

Unfortunately, no single crystal could be isolated for the " CrRu_6B_3 " phase so that its exact composition and structure cannot be unambiguously determined. Nevertheless, single crystals have been found for the quaternaries, whose structure refinement results will be described below. Furthermore, energy dispersive X-ray analysis (EDX) was very important for the determination of the Rh/Ru-ratio because this ratio cannot be determined using X-ray diffraction. As already demonstrated in other systems containing ruthenium and rhodium, e.g., in $\text{Sc}_2\text{FeRu}_{5-n}\text{Rh}_n\text{B}_2$ and $\text{Ti}_2\text{FeRu}_{5-n}\text{Rh}_n\text{B}_2$, [9] EDX analysis has delivered, here too, excellent results (see Table 2 and Fig. S2 in the

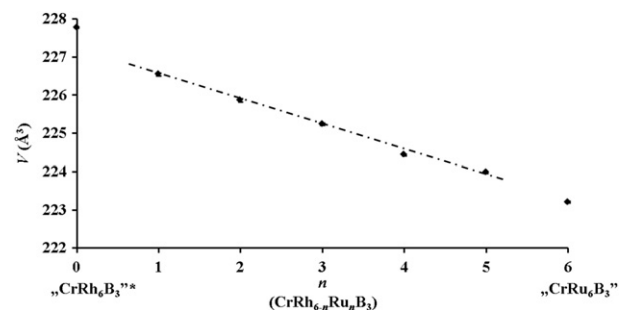


Fig. 2. Unit cell volume (V) as a function of the ruthenium content (n) in the ideal loaded composition " $\text{CrRh}_{6-n}\text{Ru}_n\text{B}_3$ ($0 \leq n \leq 6$)". The dotted line represents the linear relationship of the Vegard's law. * result from Ref. [7].

Table 2
Measured Cr/Rh/Ru ratio from EDX analysis and the derived metal compositions.

Loaded metal composition	Measured ratio (%)			EDX metal composition
	Cr	Rh	Ru	
CrRh_5Ru	14(2)	71(4)	15(2)	$\text{Cr}_{1.0(1)}\text{Rh}_{5.0(3)}\text{Ru}_{1.0(1)}$
CrRh_4Ru_2	13(1)	54(3)	33(2)	$\text{Cr}_{0.9(1)}\text{Rh}_{3.8(2)}\text{Ru}_{2.3(2)}$
CrRh_3Ru_3	12(1)	52(3)	36(2)	$\text{Cr}_{0.9(1)}\text{Rh}_{3.6(2)}\text{Ru}_{2.5(2)}$
CrRh_2Ru_4	14(1)	22(1)	64(3)	$\text{Cr}_{1.0(1)}\text{Rh}_{1.5(1)}\text{Ru}_{4.5(3)}$
CrRhRu_5	14(1)	12(1)	75(4)	$\text{Cr}_{1.0(1)}\text{Rh}_{0.8(1)}\text{Ru}_{5.2(3)}$

supporting information). The most important information from this analysis is the successful synthesis of a quaternary series containing ruthenium and rhodium and the clear distinguishable Rh-rich and Ru-rich regions of the phase (see Table 2). These two regions have the potential to structurally behave differently, as explained already in the introduction.

2.2. Structural chemistry

The central motivation of this work is the structural characterization of a series of compounds, in which two neighbors (ruthenium and rhodium) in the periodic table of elements share three crystallographic sites but still allow a third one (chromium) to mix with them, but preferentially in one or two of these sites depending on the Rh/Ru ratio. Single crystals were isolated from the quaternary loaded compositions " $\text{CrRh}_{6-n}\text{Ru}_n\text{B}_3$ ($n=1, 2$ and 4)", hence allowing the study of the structural behavior in the Rh-rich and Ru-rich regions of this phase.

The indexing routine of the single crystal data indicated the expected hexagonal unit cell (space group $P6_3mc$, no. 186, $Z=2$) in all three cases. The lattice parameters of the investigated compounds were very close to those obtained from the powder analysis (compare Tables 1 and 3) already indicating that the single-crystal composition is not far from the bulk powder composition. All relevant crystallographic data and experimental details of the data collection for the investigated compounds are

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