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# Valence-Electron-Driven Ru/Ti Site Preference in the New Ternary Boride $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ : Synthesis and Single-Crystal Structure Refinement

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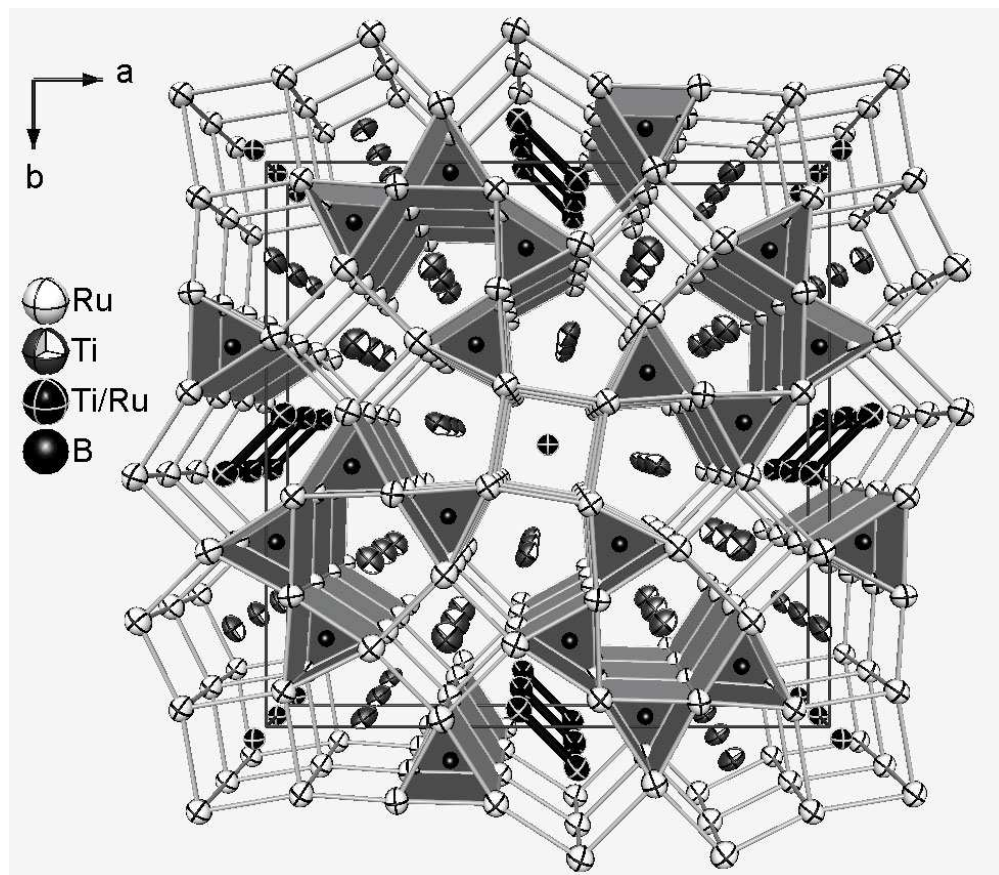


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Allgemeine Chemie

**Valence-Electron-Driven Ru/Ti Site Preference in the New  
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Structure Refinement**

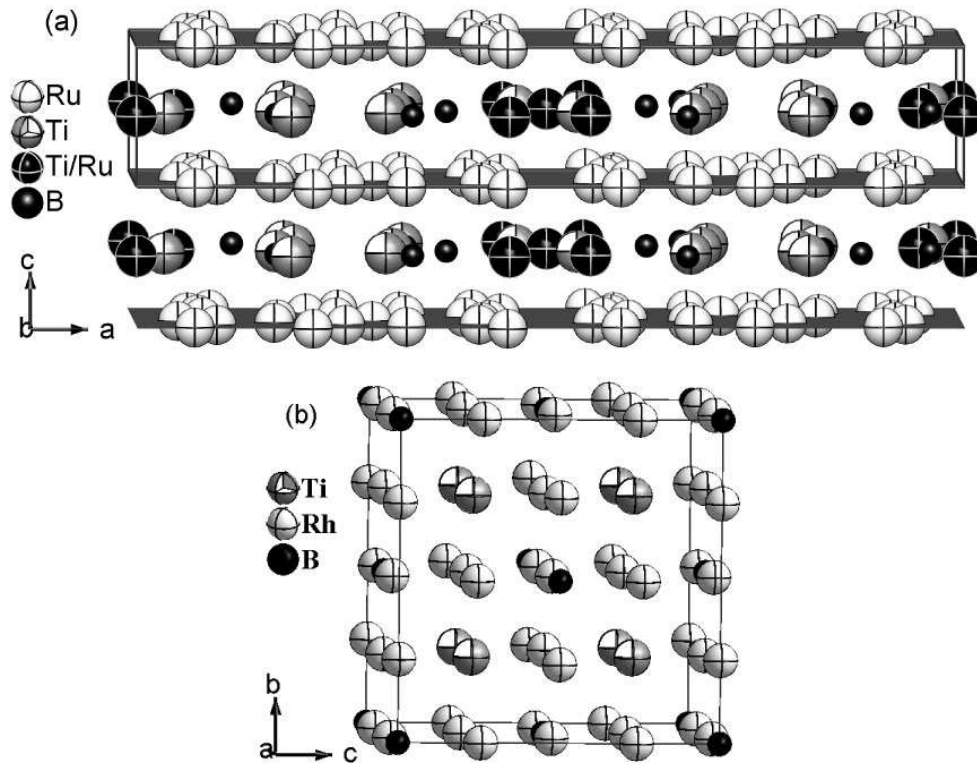
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|                               |   |





36 Perspective view along [001] of the crystal structure of  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ . Boron centered trigonal prisms  
37 and (Ti/Ru)<sub>2</sub>-dumbbells (black bonds) are highlighted. The ellipsoids are drawn at 99.9% probability  
38 level.

39 258x225mm (96 x 96 DPI)



(a) Projection nearly along  $[010]$  of the crystal structure of  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ : Ruthenium planes perpendicular to  $[001]$  are highlighted. (b) Projection nearly along  $[100]$  of the crystal structure of  $\text{Ti}_2\text{Rh}_6\text{B}$ : All planes are observed in three directions.

233x185mm (96 x 96 DPI)

## Full Paper

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### Valence-Electron-Driven Ru/Ti Site Preference in the New Ternary Boride $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ : Synthesis and Single-Crystal Structure Refinement

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**Abstract.** Powder samples and single crystals of  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$  were synthesized by arc-melting the elements in a water-cooled copper crucible under an argon atmosphere and characterized by single-crystal X-Ray diffraction and energy-dispersive X-ray analysis. The new silver-like compound crystallizes in the tetragonal system with the  $\text{Zn}_{11}\text{Rh}_{18}\text{B}_8$ -type structure (space group  $P4/mbm$  (no. 127),  $Z = 2$ ;  $a = 17.591(5)$  Å,  $c = 2.9645(13)$  Å,  $R_1 = 0.0708$ ,  $wR_2 = 0.0992$ ,  $GooF = 1.047$  for all 1266 reflections and 58 parameters). The interesting characteristic in this new ternary variant is the valence electron driven site-preferential mixture of both titanium and ruthenium forming “ladders” along the [001] direction.

**Keywords:** Transition-metal borides,  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ , crystal structure,  $\text{Zn}_{11}\text{Rh}_{18}\text{B}_8$ -type, valence electrons

### Introduction

Recently we reported the first ferromagnetic transition metal boride containing ladders of a magnetically active element (iron),  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$  [1]. Other quaternary derivatives of the  $\text{Zn}_{11}\text{Rh}_{18}\text{B}_8$ -type structure,  $\text{Zn}_{10}\text{MRh}_{18}\text{B}_8$  ( $M = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ ) [2] have also been reported but they contain the well documented one dimensional chains of a magnetically active element  $M$  [3-7]. In fact substituting either zinc in  $\text{Zn}_{11}\text{Rh}_{18}\text{B}_8$ , or titanium in a hypothetical “ $\text{Ti}_{11}\text{Ru}_{18}\text{B}_8$ ” by iron, leads to the different local structures observed. In the

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3 ternaries  $Zn_{11}Rh_{18}B_8$  and hypothetical " $Ti_{11}Ru_{18}B_8$ " both zinc and titanium atoms occupy  
4 tetragonal, pentagonal and elongated hexagonal prisms of rhodium or ruthenium atoms,  
5 respectively, with the elongated hexagonal prisms accommodating two atoms (as  
6 "dumbbells"). In terms of volume, one-half of the elongated hexagonal prism, i.e. the volume  
7 accommodating only one atom of the dumbbell, is smaller than a single pentagonal prism, but  
8 larger than a tetragonal prism. Consequently, if atomic size factors are influential for the  
9 stability of these compounds, substituting zinc and titanium by iron, respectively, in  
10  $Zn_{11}Rh_{18}B_8$  and " $Ti_{11}Ru_{18}B_8$ " should give the same result, since both zinc (atomic radius,  
11  $r_a = 1.31 \text{ \AA}$ ) and titanium ( $r_a = 1.38 \text{ \AA}$ ) are clearly larger than iron ( $r_a = 1.25 \text{ \AA}$ ). However,  
12 different substitution patterns emerge:  $Zn_{10}FeRh_{18}B_8$  finds iron replacing zinc atoms in the  
13 smallest tetragonal prism, as expected from size considerations; whereas in  $Ti_9Fe_2Ru_{18}B_8$ , iron  
14 has replaced titanium preferentially and unexpectedly in the elongated hexagonal prisms.  
15 Therefore, electronic factors should play a key role in understanding the substitution  
16 preference of titanium by iron in hypothetical " $Ti_{11}Ru_{18}B_8$ ", leading to  $Ti_9Fe_2Ru_{18}B_8$  [1]. The  
17 present work deals with the synthesis and structural characterization of the hypothetical  
18 " $Ti_{11}Ru_{18}B_8$ ". A successful synthesis should lead not only to the first phase in the Ti–Ru–B  
19 system, but also to a better understanding of the substitution preference mentioned above.  
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## 35 Experimental Section

### 36 *Synthesis*

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39 The title compound was synthesized by arc-melting the elements in a water-cooled copper  
40 crucible under an argon atmosphere using a tungsten tip as a second electrode. The starting  
41 elements, titanium (pieces, 99.9 %, Degussa), ruthenium (powder, 99.9%, Umicore) and  
42 boron (pieces, 99.999%, Alfa Aesar) were weighed in the atomic ratio 11:18:8 according to  
43 the hypothetical formula " $Ti_{11}Ru_{18}B_8$ ". In another synthesis ruthenium was used in excess  
44 (50% more, ratio 11:27:8). The well homogenized educts were pressed into pellets and arc-  
45 melted under argon. The argon was purified over silica gel, molecular sieves, and titanium  
46 sponge (950 K). Weight losses during the melting process were negligible. A silver-like  
47 product with metallic luster containing some single crystals (only in the second synthesis)  
48 suitable for X-ray structure analysis was obtained. These needle-shaped crystals could easily  
49 be isolated manually under an optical microscope for X-ray single-crystal analysis. Powder  
50 diffractograms of the silver-like products were taken using a Guinier powder diffractometer  
51 with  $Cu-K\alpha_1$  radiation ( $\lambda = 1.54059 \text{ \AA}$ ) and silicon as an internal standard. Phase analyses and  
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3 lattice parameter refinements were carried out using the program WINXPOW [8]. The  
4 presence of the two metals and their ratio were characterized by Energy Dispersive X-ray  
5 analysis (EDX) on a high-resolution, low-energy SEM of the type LEO 1530 (Oberkochen,  
6 Germany) equipped with an EDX system of the type INCA (Oxford, England). EDX  
7 measurements on several selected crystals provided the ratio 1:1.92 (Ti:Ru) (averaged  
8 experimental data) for crystals obtained from the second synthesis.  
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### 14 15 16 ***Crystal Structure Determination***

17 Two single crystals of suitable sizes were fixed in glass capillaries and data were collected on  
18 a CCD single crystal diffractometer (Bruker SMART APEX) with graphite-monochromatized  
19 Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The X-ray intensities were corrected for absorption using a  
20 semi-empirical procedure [9]. The crystal structure was refined by full-matrix least squares  
21 refinement [10], based on  $F^2$ , using anisotropic displacement parameters for all metals (Ti,  
22 Ru) and isotropic ones for B. The initial structure file of  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$  (starting model) was  
23 first transformed to the standard setting using the program SETSTRU from the Bilbao  
24 Crystallographic Server [11]. All relevant crystallographic data and experimental details of  
25 the data collection are listed in Table 1. Table 2 contains the atomic coordinates and  
26 displacement parameters, while Table 3 summarizes selected interatomic distances. Crystal  
27 structure drawings were produced using the program *Diamond* [12]. A listing of all  
28 refinement data and data collection is available <sup>1)</sup>.  
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40 1): More details on the structure determination may be obtained from the Fachinformationszentrum Karlsruhe (e-  
41 mail address: [crysdata@fiz-karlsruhe.de](mailto:crysdata@fiz-karlsruhe.de)), D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the CSD  
42 depository number: CSD 420561  
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## 46 47 **Results and Discussion**

### 48 49 50 ***Phase analysis***

51 From phase analyses of the powder data, the expected  $\text{Zn}_{11}\text{Rh}_{18}\text{B}_8$ -type phase could easily be  
52 identified either for 11:18:8 (Ti:Ru:B) or for 11:27:8 starting compositions. In the first case  
53 the expected phase was only the second component (about 30% yield), as cubic TiRu [13]  
54 was found to be the main phase. Because this synthesis was not successful as hoped, we  
55 started a second synthesis using ruthenium in excess because from size and electronic  
56 (Valence electrons, VE) considerations ruthenium is nearer to iron than titanium (note that the  
57 starting point for this work was  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$  where iron was substituted by titanium). As a  
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consequence, the yield of the expected phase could be increased to about 80%, with hexagonal  $\text{Ti}_{0.1}\text{Ru}_{0.9}$  [13] identified as the second phase. The presence of ruthenium in the second phase could be expected (used in excess) but not titanium. Although only in small amount the presence of titanium in the second phase ( $\text{Ti}_{0.1}\text{Ru}_{0.9}$ ) indicates that we may expect less titanium in the main phase. In both syntheses some small unidentified intensities were present in the powder diffractograms. Nevertheless the lattice parameters [ $(a = 17.557(5) \text{ \AA}, c = 2.9731(8) \text{ \AA}, V = 916.4(6) \text{ \AA}^3$ ) and  $(a = 17.560(5) \text{ \AA}, c = 2.9603(8) \text{ \AA}, V = 912.8(6) \text{ \AA}^3$ )] could be refined, respectively for the first and second synthesis. The volume difference is  $3.6 \text{ \AA}^3$  indicating a higher titanium/ruthenium ratio in the product from the first synthesis than from the second, and therefore a phase width. However this homogeneity range can only be studied using single crystals because of the presence of side products in the powder samples. Single crystals were found only in the second experiment and, given the excess of ruthenium used, it is expected that the maximum amount of ruthenium that may enter the structure will be determined. From the crystals obtained, two were suitable for single-crystal structure analysis.

### ***Structure refinement***

The standardized  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$  structure was used as starting model for the single-crystal structure refinements, but replacing iron by titanium, thus the starting composition was “ $\text{Ti}_{11}\text{Ru}_{18}\text{B}_8$ ”. After a few refinement cycles, the structure type was confirmed but the refinement did not converge. In fact, in the difference Fourier map a high peak ( $21.05 \text{ e/\AA}^3$ ) was found at only  $0.04 \text{ \AA}$  far from the fifth titanium site (Ti5,  $4h$ , i.e. the iron site in  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$ ). Furthermore, the displacement parameters of Ti5 were meaningless (too small compared to the other titanium sites and non positive definite). All these discrepancies suggested that this site needs more electrons. However a refinement using the electron richer ruthenium alone at the Ti5 site also leads to bad results (with very large displacement parameters). Good results were then achieved after refining with both ruthenium and titanium at the Ti5 position (mixed occupancy refinement), and this leads to the highest and lowest peaks in the difference Fourier map of only  $3.25 \text{ e/\AA}^3$  and  $-2.41 \text{ e/\AA}^3$  respectively. The refinements did converge at this point (for both single crystals) but the displacement parameters of one titanium atom (Ti2, site  $2b$ ) were not fully satisfactory as they were a bit smaller than those of the other titanium atoms. A mixed occupancy refinement was therefore used also for this site: Although the  $R$ -values did not change at this point, the displacement parameters for the  $2b$  site improved significantly. In the final proper refinement ( $R_1 = 0.071$ ,



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3  $wR_2 = 0.099$  for all 1269 reflections, 58 parameters and no restraint) the overall occupancies  
4 for Ti5/Ru6 and Ti2/Ru7 sites were constrained to unity and the individual occupancies were  
5 refined to 0.538(13)/0.462(13) for Ti5/Ru6 and 0.970(16)/0.030(16) for Ti2/Ru7, leading to  
6 the formula  $\text{Ti}_{10.05(4)}\text{Ru}_{18.95(4)}\text{B}_8$ . Nearly the same composition was obtained from the second  
7 single crystal ( $\text{Ti}_{10.03(4)}\text{Ru}_{18.97(4)}\text{B}_8$ ) as expected from phase analysis. Therefore the formula  
8  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$  may be retained within experimental error for this phase and will be used in the  
9 following. These results were in full agreement with EDX analyses on several crystals (see  
10 experimental part), inducing that a maximum of 19 ruthenium atoms may enter the structure.  
11 Nevertheless another study will be needed to identifying the phase width  $x$  of  $\text{Ti}_{11-x}\text{Ru}_{18+x}\text{B}_8$ :  
12 Precisely, to determine the maximal amount of titanium that may enter this structure.  
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23 -----Figure 1-----  
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### 26 **Structural chemistry**

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28  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$  crystallizes, like  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$ ,  $\text{Zn}_{11}\text{Rh}_{18}\text{B}_8$  and  $\text{Zn}_{10}\text{MRh}_{18}\text{B}_8$  ( $M = \text{Sc} - \text{Cu}, \text{Al}, \text{Si},$   
29  $\text{Ge}, \text{Sn}$ ), in the tetragonal system in space group  $P4/mbm$ . Its crystal structure deviates from  
30  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$  structure mainly because the  $\text{Fe}_2$ -ladder subunit is replaced by the  $(\text{Ti5/Ru6})_2$ -  
31 ladder, thus reducing the number of valence electrons (VE) from 220 ( $4 \times 9 + 8 \times 2 + 8 \times 18 +$   
32  $3 \times 8 = 220$ ) for  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$  to 216 for  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ . The hypothetical and originally targeted  
33 “ $\text{Ti}_{11}\text{Ru}_{18}\text{B}_8$ ” composition has 212 VE i.e. 4 VE less than the synthesized  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ ,  
34 suggesting that the iron position in  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$  structure may not be fully substituted by  
35 elements with a number of VE smaller than that of iron by at least four electrons (e.g. Ti, Sc,  
36 ...). In other words the number of VE of titanium is not sufficient to fulfill the requirements  
37 (bonding to itself and to the neighboring atoms) needed for this site. From a theoretical point  
38 of view it was deduced, via the pseudogap observed in the calculated density of states of  
39  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$ , that its structure could accommodate even more valence electrons (up to 13  
40 VE) [1]. This deduction may open the way for the synthesis of electron richer compounds  
41 crystallizing with the same structure type (this study is being done). Then again, the theory  
42 does not give the VE number at which the structure will collapse if we remove some electrons,  
43 thereby destabilizing this structure type. The actual result ( $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ , 216 VE) suggests that  
44 four VE may be removed from  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$  (220 VE) without destroying the structure.  
45 Attempts to decrease even more the number of VE by replacing titanium with scandium are  
46 underway.  
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3 By comparing  $Zn_{11}Rh_{18}B_8$  with  $Ti_{10}Ru_{19}B_8$  it becomes clear why different substitution  
4 patterns occur en route to the quaternaries  $Zn_{10}FeRh_{18}B_8$  and  $Ti_9Fe_2Ru_{18}B_8$ . In the two ternary  
5 phases zinc and titanium are present at the same sites with the exception of the  $4h$  site where  
6  $Zn_{2-}$  and  $(Ti_5/Ru_6)_2$ -dumbbells are found: In fact all tetragonal and pentagonal prisms present  
7 in  $Zn_{11}Rh_{18}B_8$  and  $Ti_{10}Ru_{19}B_8$  (built up by rhodium and ruthenium, respectively) are centered  
8 respectively by zinc or titanium, although both prisms are the smallest and the largest  
9 available for the two elements (see figure 1). The middle-sized prism (elongated hexagonal  
10 prism) is also centered as expected by zinc in  $Zn_{11}Rh_{18}B_8$  but not by titanium alone in  
11  $Ti_{10}Ru_{19}B_8$ . From size considerations one would also expect titanium alone at this  $4h$  site,  
12 since both zinc (atomic radius,  $r_a = 1.31 \text{ \AA}$ ) and titanium ( $r_a = 1.38 \text{ \AA}$ ) are clearly larger than  
13 iron ( $r_a = 1.25 \text{ \AA}$ ) [14]. The fact that titanium can only fill the  $4h$  site together with the  
14 electron richer but smaller ruthenium is the proof, that this site needs more valence electrons  
15 than the four available for titanium. Therefore, the syntheses of the stoichiometric quaternary  
16 derivatives “ $Ti_9M_2Ru_{18}B_8$ ” ( $M = Cr - Zn$ ) should be possible because at this  $4h$  site more  
17 valence electrons will be available from the M-elements compared to titanium. On the  
18 contrary, the synthesis of stoichiometric “ $Ti_9Sc_2Ru_{18}B_8$ ” should not be possible. The VE  
19 driven site preference observed in the Ti-based phases, particularly for the  $4h$  site, is the main  
20 difference if compared with the Zn-based phases of the  $Zn_{11}Rh_{18}B_8$  structure type. It is also  
21 the main reason why stoichiometric “ $Ti_{11}Ru_{18}B_8$ ” is not accessible experimentally. Attempts  
22 to synthesize the  $Zn_{10}FeRh_{18}B_8$ -related “ $Ti_{10}FeRu_{18}B_8$ ” also failed, as expected.

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The COHP analysis performed for  $Ti_9Fe_2Ru_{18}B_8$ , suggested, that it is the heteroatomic Ru–B  
and Ru–Ti bonds that create its structural stability [1]. The new ternary isotype  $Ti_{10}Ru_{19}B_8$  is  
expected to be also stabilized by these two bonds, because the distances observed in both  
phases are quite similar, even the distance in the  $Fe_2$ -dumbbell ( $2.49 \text{ \AA}$ ) is nearly the same as  
that of the unexpected  $(Ti_5/Ru_6)_2$ -dumbbell ( $2.46 \text{ \AA}$ ).

The relatively short Ru–B distances, ranging from  $2.16 \text{ \AA}$  to  $2.22 \text{ \AA}$  (average,  $2.19 \text{ \AA}$ , see  
table 3) are only slightly longer than the sum of their covalent radii ( $2.07 \text{ \AA}$ ), suggesting very  
strong bonding interactions. Similar Ru–B interatomic distances are found in the phases  
 $Ru_2B_3$  (average,  $2.18 \text{ \AA}$ ) [15],  $Fe_xRu_{7-x}B_3$  ( $0 < x \leq 1.5$ ; average,  $2.14 \text{ \AA}$ ) [16],  $Ti_{1.6}Os_{1.4}RuB_2$   
( $2.16 \text{ \AA}$ ) [17] and of course  $Ti_9Fe_2Ru_{18}B_8$  (average,  $2.18 \text{ \AA}$ ). As said before, strong bonding is  
also expected for the Ti–Ru interaction, and this is reflected in the average distance ( $2.71 \text{ \AA}$ )  
being nearly the same as the sum of their metallic radii for CN 8 (ca.  $2.72 \text{ \AA}$ ) [14]. The  
average Ru–M ( $M = Ti_5/Ru_6$ ) distance of  $2.75 \text{ \AA}$  lies, as could be expected, between the sum  
of the metallic radii for CN 12 for Ru–Ti ( $2.80 \text{ \AA}$ ) and Ru–Ru ( $2.67 \text{ \AA}$ ) [14]. As a

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3 consequence of these significant heteroatomic interactions between Ru atoms and the other  
4 elements, homoatomic Ru–Ru interactions are expected to be weaker than in elemental Ru,  
5 because greater electron densities are engaged in Ru–X (X = B, Ti, Ti/Ru) bonds. As expected  
6 a wide range of Ru–Ru distances is observed in  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ , with an average of 2.85 Å that is  
7 significantly longer than the ruthenium metallic distance for CN12 (2.67 Å) [14]. The  
8 (Ti/Ru)<sub>2</sub>-dumbbell has a rather short distance, 2.46 Å, which is shorter than the sum of the  
9 metallic radii for CN 12 for Ru–Ru (2.67 Å) and Ti–Ti (2.93 Å). Therefore strong bonding is  
10 expected as observed for Fe<sub>2</sub>-dumbbell (2.49 Å) in  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$ .

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12 No significant interactions were found for Ti–(Ti/Ru) and Ti–B contacts in the structure.  
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21 -----Figure 2-----  
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24 ***Comparison with other ternary transition-metal-rich borides containing at least one of the***  
25 ***two metals***  
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28  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$  is the first compound in the Ti–Ru–B system. In fact, only fourteen ternary  
29 transition-metal-rich borides are known so far, which contain at least one of the two metals:  
30 From these fourteen, four borides contain titanium and ten contain ruthenium. They can be  
31 divided in two groups:  
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34 a) In the first group a preferred orientation is observed in their crystal structures: A layer-like  
35 arrangement of all atoms into two different sheets perpendicular to only one direction.  
36  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$  meets exactly this requirement (see figure 2a), and is therefore structurally related  
37 to  $\text{Ti}_3\text{Co}_5\text{B}_2$ ,  $\text{Ti}_2\text{ReB}_2$  ( $\text{U}_3\text{Si}_2$  type),  $\text{YRu}_3\text{B}_2$  ( $\text{CeCo}_3\text{B}_2$ -type), and  $\text{Sc}_2\text{Ru}_5\text{B}_4$  [18]. In all these  
38 cases the most represented metal builds one layer, which connects to the identical adjacent  
39 one, thereby building prisms in which the other metal and boron are located (see for example  
40 figure 1).  
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43 b) A three dimensional arrangement of all atoms without any preferred orientation forms the  
44 second group. The ten remaining ternary transition-metal-rich borides (from the fourteen  
45 mentioned above) fulfil this requirement (see for example figure 2b): The double perovskite-  
46 like  $\text{Ti}_2\text{Rh}_6\text{B}$  [19], the  $\tau$ -borides ( $\text{Ti}_2\text{M}_{21}\text{B}_6$ ,  $\text{Ti}_3\text{M}_{20}\text{B}_6$  M = Co, Ni; and  $\text{Ta}_{3.25}\text{Ru}_{19.75}\text{B}_6$ , all  
47  $\text{Cr}_{23}\text{C}_6$ -type) [18], the Th<sub>7</sub>Fe<sub>3</sub>-type  $\text{Fe}_x\text{Ru}_{7-x}\text{B}_3$  [16],  $\text{W}_{1.75}\text{Ru}_{1.25}\text{B}_2$  ( $\text{Mo}_2\text{IrB}_2$ -type), and  
48  $\text{MRu}_4\text{B}_4$  (M = Y, Sc) [18] did not show any preferred orientation and are therefore  
49 structurally not related to  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ .  
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## Conclusion

The new phase  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$  was successfully synthesized (as polycrystalline sample and single crystals) from the elements and characterized by X-ray single-crystal analysis and EDX measurements. It is the first ternary compound in the Ti-Ru-B system.  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$  crystallizes as a substitutional variant of the  $\text{Zn}_{11}\text{Rh}_{18}\text{B}_8$ -type structure, and a valence electron driven site preference is observed for the Ru/Ti mixture.

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27 **Figure 1.** Perspective view along [001] of the crystal structure of  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ . Boron centered  
28 trigonal prisms and  $(\text{Ti}/\text{Ru})_2$ -dumbbells (black bonds) are highlighted. The ellipsoids are  
29 drawn at 99.9% probability level.  
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36 **Figure 2.** (a) Projection nearly along [010] of the crystal structure of  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ : Ruthenium  
37 planes perpendicular to [001] are highlighted. (b) Projection nearly along [100] of the crystal  
38 structure of  $\text{Ti}_2\text{Rh}_6\text{B}$ : All planes are observed in three directions.  
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**Table 1**Crystallographic and structure refinement data for  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ .

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|--|--|
| Formula  | $\text{Ti}_{10.05(4)}\text{Ru}_{18.95(4)}\text{B}_8$                                       |
| Formula Weight ( $\text{g}\cdot\text{mol}^{-1}$ );   | 2483.42;   |
| $F(000)$   | 2190   |
| Crystal size ( $\text{mm}^3$ )                       | $0.10 \times 0.03 \times 0.03$   |
| Space group; $Z$                                     | $P4/mbm$ (No. 127); 2  |
| Lattice parameters                                   | $a = 17.591(5) \text{ \AA}$ , $c = 2.9645(13) \text{ \AA}$<br>$V = 917.4(6) \text{ \AA}^3$ |
| Calc. density ( $\text{g}\cdot\text{cm}^{-3}$ )      | 8.99   |
| Abs. Correction                                      | Semi-empirical   |
| Abs. Coefficient ( $\text{mm}^{-1}$ )                | 19.13  |
| $T_{\text{min}}$ ; $T_{\text{max}}$                  | 0.251; 0.598   |
| Diffractionmeter                                     | Bruker APEX CCD, Mo $K\alpha$ ,<br>graphite monochromator                                  |
| $\theta$ -range                                      | $4.78^\circ < \theta < 36.01^\circ$  |
| $hkl$ -range   | $-28 \leq h \leq 17$<br>$-28 \leq k \leq 28$<br>$-4 \leq l \leq 4$                         |
| No. reflections; $R_{\text{int}}$                    | 9877; 0.0787   |
| No. independent reflections                          | 1266   |
| No. parameters                                       | 58   |
| Refinement   | <i>SHELX-97</i> , full matrix against $F^2$  |
| $R_1$ ; $wR_2$ (all $I$ )                            | 0.0708; 0.0992   |
| <i>GooF</i>  | 1.047  |
| Diff. peak / hole ( $\text{e}\cdot\text{\AA}^{-3}$ ) | 3.253 / -2.415   |

**Table 2**Atomic coordinates and equivalent displacement parameters ( $\text{\AA}^2$ ) for  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ 

| Atom     | <i>x</i>   | <i>y</i>   | <i>z</i> | Wyckoffsite | Occupancy     | $U_{\text{eq}}^{[a]}/U_{\text{iso}}$ |
|----------|------------|------------|----------|-------------|---------------|--------------------------------------|
| Ru1      | 0.91930(4) | 0.25328(4) | 0        | 8 <i>i</i>  | 1.0           | 0.0068 (2)                           |
| Ru2      | 0.91502(4) | 0.41502(4) | 0        | 4 <i>g</i>  | 1.0           | 0.0068(2)                            |
| Ru3      | 0.05292(4) | 0.32597(4) | 0        | 8 <i>i</i>  | 1.0           | 0.0083(2)                            |
| Ru4      | 0.78805(4) | 0.16841(4) | 0        | 8 <i>i</i>  | 1.0           | 0.0080(2)                            |
| Ru5      | 0.93043(4) | 0.09787(4) | 0        | 8 <i>i</i>  | 1.0           | 0.0066(2)                            |
| Ti1      | 0.8032(1)  | 0.3032(1)  | 1/2      | 4 <i>h</i>  | 1.0           | 0.0081(4)                            |
| Ti2/ Ru7 | 0          | 0          | 1/2      | 2 <i>b</i>  | 0.97(2)/ 0.03 | 0.0069(9)                            |
| Ti3      | 0.0352(1)  | 0.18689(9) | 1/2      | 8 <i>j</i>  | 1.0           | 0.0074(3)                            |
| Ti4      | 0.1718 (1) | 0.3282(1)  | 1/2      | 4 <i>h</i>  | 1.0           | 0.0129(5)                            |
| Ti5/ Ru6 | 0.04937(6) | 0.45063(6) | 1/2      | 4 <i>h</i>  | 0.54(2)/ 0.46 | 0.0109(5)                            |
| B1       | 0.8775(6)  | 0.1698(6)  | 1/2      | 8 <i>j</i>  | 1.0           | 0.010(2)                             |
| B2       | 0.9627(6)  | 0.3339(6)  | 1/2      | 8 <i>j</i>  | 1.0           | 0.009(2)                             |

[a]:  $U_{\text{eq}}$  is defined as 1/3 of the trace of the orthogonalized  $U_{ij}$  tensors;  $U_{\text{iso}}$  only for boron

**Table 3**  
Selected bond lengths (Å) for  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ .

| site <i>i</i> | site <i>j</i> | $d_{ij}$ | Coordination <sup>[b]</sup> | site <i>i</i> | site <i>j</i> | $d_{ij}$ | coordination <sup>[b]</sup> |
|---------------|---------------|----------|-----------------------------|---------------|---------------|----------|-----------------------------|
| Ru1           | B2            | 2.189(8) | 2                           | Ru5           | Ti3           | 2.770(2) | 2                           |
|               | B1            | 2.212(8) | 2                           |               | Ru4           | 2.795(2) | 1                           |
|               | Ti1           | 2.672(2) | 2                           |               | Ti3           | 2.836(2) | 2                           |
|               | Ru3           | 2.676(2) | 1                           |               | Ru5           | 2.964(2) | 2                           |
|               | Ru5           | 2.741(2) | 1                           | Ti1           | Ru1           | 2.672(2) | 4                           |
|               | Ru4           | 2.749(2) | 1                           |               | Ru4           | 2.808(2) | 4                           |
|               | Ti3           | 2.778(2) | 2                           |               | Ti1           | 2.964(2) | 2                           |
|               | Ru2           | 2.846(2) | 1                           |               | Ti2/Ru7       | Ru5      | 2.580(1)                    |
| Ru1           | 2.964(2)      | 2        | Ti2/Ru7                     | 2.964(2)      |               | 2        |                             |
| Ru2           | B2            | 2.223(8) | 4                           | Ti3           | Ru5           | 2.770(2) | 2                           |
|               | Ru1           | 2.846(2) | 2                           |               | Ru1           | 2.778(2) | 2                           |
|               | Ti5/Ru6       | 2.859(1) | 4                           |               | Ru4           | 2.808(2) | 2                           |
|               | Ru3           | 2.888(2) | 2                           |               | Ru5           | 2.836(2) | 2                           |
| Ru3           | Ru2           | 2.964(2) | 2                           | Ru3           | 2.878(2)      | 2        |                             |
|               | B2            | 2.175(8) | 2                           | Ti3           | 2.964(2)      | 2        |                             |
|               | Ti4           | 2.563(2) | 2                           | Ti4           | Ru4           | 2.527(2) | 4                           |
|               | Ru5/Ti6       | 2.648(2) | 2                           |               | Ru3           | 2.563(2) | 4                           |
|               | Ru1           | 2.676(2) | 1                           |               | Ti4           | 2.964(2) | 2                           |
|               | Ru4           | 2.855(2) | 1                           |               | Ti5/Ru6       | Ti5/Ru6  | 2.456(3)                    |
|               | Ti3           | 2.878(2) | 2                           | Ru3           |               | 2.648(2) | 4                           |
|               | Ru2           | 2.888(2) | 1                           | Ru2           |               | 2.859(1) | 4                           |
| Ru3           | 2.964(2)      | 2        | Ti5/Ru6                     | 2.964(2)      |               | 2        |                             |
| Ru4           | B1            | 2.162(8) | 2                           | B1            | Ru5           | 2.160(8) | 2                           |
|               | Ti4           | 2.527(2) | 2                           |               | Ru4           | 2.162(8) | 2                           |
|               | Ru5           | 2.795(2) | 1                           |               | Ru1           | 2.212(8) | 2                           |
|               | Ti3           | 2.808(2) | 2                           | B2            | Ru3           | 2.175(8) | 2                           |
|               | Ti1           | 2.808(2) | 2                           |               | Ru1           | 2.189(8) | 2                           |
|               | Ru3           | 2.855(2) | 1                           |               | Ru2           | 2.223(8) | 2                           |
| Ru4           | 2.964(2)      | 2        |                             |               |               |          |                             |
| Ru5           | B1            | 2.160(8) | 2                           |               |               |          |                             |
|               | Ti2/Ru7       | 2.580(1) | 2                           |               |               |          |                             |

[b]: number of equivalent contacts between these two sites