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New ternary tantalum borides containing boron dumbbells: Experimental and theoretical studies of Ta_2OsB_2 and TaRuB

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ABSTRACT

The new ternary transition metal-rich borides Ta_2OsB_2 and TaRuB have been successfully synthesized by arc-melting the elements in a water-cooled crucible under an argon atmosphere. The crystal structures of both compounds were solved by single-crystal X-ray diffraction and their metal compositions were confirmed by EDX analysis. It was found that Ta_2OsB_2 and TaRuB crystallize in the tetragonal Nb_2OsB_2 (space group *P*4/*mnc*, no. 128) and the orthorhombic NbRuB (space group *Pmma*, no. 51) structure types with lattice parameters $a=5.878(2)$ Å, $c=6.857(2)$ Å and $a=10.806(2)$ Å, $b=3.196(1)$ Å, $c=6.312(2)$ Å, respectively. Furthermore, crystallographic, electronic and bonding characteristics have been studied by density functional theory (DFT). Electronic structure relaxation has confirmed the crystallographic parameters while COHP bonding analysis indicates that B_2-dummbells are the strongest bonds in both compounds. Moreover, the formation of osmium dumbbells in Ta_2OsB_2 through a *Peierls* distortion along the *c*-axis, is found to be the origin of superstructure formation. Magnetic susceptibility measurements reveal that the two phases are Pauli paramagnets, thus confirming the theoretical DOS prediction of metallic character. Also hints of superconductivity are found in the two phases, however lack of single phase samples has prevented confirmation. Furthermore, the thermodynamic stability of the two modifications of AMB (A=Nb, Ta; M =Ru, Os) are studied using DFT, as new possible phases containing either B_4- or B_2-units are predicted, the former being the most thermodynamically stable modification.
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1. Introduction

Niobium and tantalum, elements of the 5th group in the periodic table were discovered early in the nineteenth century, but until the middle of the nineteenth century it was still unclear if they were two different elements due to their very similar chemical properties and similar values of the metallic and ionic radii [1]. Niobium- and tantalum-based solid state compounds like oxides, carbides, or nitrides usually crystallize in a very similar crystal structure and they find many technological applications as oxygen sensors, waveguides or as tunnel barriers in Josephson tunnel junctions [2–4]. The crystal structures of binary and ternary transition metal borides of these elements were characterized over the last six decades [5]. For the binary monoborides NbB and TaB with orthorhombic CrB-type structure superconductivity was found below 8.25 K and 4 K, respectively [6,7], but for the diborides NbB_2 and TaB_2 crystallizing in the AlB_2-type structure, it is still unclear if they are superconducting materials or not [8]. Moreover, Nb_2FeB_2 and Ta_2FeB_2 crystallizing in the Mo_2FeB_2-type structure [9] are examples of ternary borides of niobium and tantalum, for which antiferromagnetic ordering of the Fe chains has been predicted [10,11]. We have recently discovered two new structure types in the M–Nb–B systems (M=Ru and Os), namely Nb_2OsB_2 (space group *P*4/*mnc*) [12] and NbRuB (space group *Pmma*) [13]. The first compound, Nb_2OsB_2, was characterized as new twofold superstructure of the Mo_2FeB_2-type [9] (U_3Si_2 family [14]), and can be viewed as a simple 1:1 intergrowth variant of strongly distorted AlB_2 ([NbB_2] motif) and CsCl ([NbOs] motif) related slabs. The second compound, NbRuB, was obtained by attempting to synthesize the hypothetical phase "*Nb_2RuB_2*", which we have predicted to crystallize with the Nb_2OsB_2-type structure [13]. This structure, which is built up by Re_3B and AlB_2 related slabs, is composed of two different layers stacked alternately along the smaller *b*-axis.

Due to the aforementioned similarities between niobium and tantalum, we have substituted Ta for Nb in Nb_2OsB_2 and NbRuB en route to the new Ta_2OsB_2 and TaRuB, for which the experimental

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and theoretical studies will be discussed in the following. Abstracts of this work, presented at conferences, were published recently [15,16]. During the preparation of this paper, the new equiatomic compounds, TaRuB and NbOsB, were reported [17] but they crystallize with the recently discovered orthorhombic $Ti_{1+x}Rh_{2-x+y}Ir_{3-y}B_3$ structure type [18].

2. Experimental

2.1. Synthesis

Samples of the title compounds were synthesized by arc-melting the elements in a water-cooled copper crucible under an argon atmosphere using tungsten tip as a second electrode. The starting materials tantalum (powder, ChemPur, 99.9%), ruthenium (powder, 99.9% Alfa Aesar), osmium (powder, ABCR, 99.9%) and boron (amorphous powder, 99.9%, ChemPur) were weighed in the respective atomic ratios with total masses of 0.3 g, pressed into pellets and arc-melted under argon atmosphere (0.2 atm) using a direct current of 40 A until homogeneous melting. Prior the usage of argon it was purified over silica gel, molecular sieves and titanium sponge (950 K). All techniques to synthetize Ta_2OsB_2 were performed inside a glove box (M. Braun, LABMASTER 130) filled with argon atmosphere because of the sensitivity of osmium to oxygen. Weight losses during the melting process were negligible. Silvery products shaped like spheres with metallic luster were obtained from the syntheses. The samples were mechanically cracked apart and needle-shaped single crystals could be isolated manually under an optical microscope.

2.2. Powder and single crystal X-ray investigations

The samples were characterized through powder patterns collected with a STOE Stadi-P powder diffractometer equipped with a Ge (111) monochromatized Cu-$K_{\alpha1}$ radiation ($\lambda = 1.54059$ Å). The lattice parameters were obtained from full-matrix least square refinement of the powder data using the Rietveld method within the FULLPROF suite [19]. The standard deviations obtained by the refinement procedure were multiplied by the SCOR-parameter according to Ref. [20]. The starting models used for the Rietveld refinements emanated from the single crystal data of previously reported Nb_2OsB_2 and NbRuB but substituting Nb with Ta.

Single crystals were found and analyzed for the synthesized phases. They were selected from the crushed samples and fixed on top of glass capillaries, and X-ray data were collected at room temperature on a CCD single-crystal diffractometer (Bruker SMART APEX) with graphite-monochromatized Mo-K_α radiation ($\lambda = 0.71073$ Å). The X-ray intensities were corrected with respect to absorption using a semi-empirical procedure [21]. The crystallographic data and experimental details are summarized in Table 1. The structure was solved by direct methods and refined (full-matrix least-squares based on F^2) by means of the SHELX programs [22], anisotropic thermal parameters were used for the metals atoms, and isotropic ones were used for the boron atoms. Table 2 contains the atomic coordinates and the displacement parameters. Selected bond lengths are given in Table 3.

2.3. Elemental analysis

Many crystals including the single crystal used for SC-XRD were investigated using high-resolution low-energy SEM of the type LEO/Zeiss 1450 VP (Oberkochen, Germany) equipped with an EDX system of the type INCA (Oxford, UK, England).

Table 1
Crystallographic and single-crystal structure refinement data of TaRuB and Ta_2OsB_2.

Formula		**TaRuB**	**Ta_2OsB_2**
Formula weight [g/mol]		292.8	573.7
$F(000)$		732	464
Crystal size [mm^3]		$0.05 \times 0.02 \times 0.01$	$0.05 \times 0.02 \times 0.02$
θ - range (deg)		$3.23 \le \theta \le 30.39$	$4.91 \le \theta \le 35.78$
hkl range		$-14 \le h \le 14$	$-9 \le h \le 9$
		$-4 \le k \le 4$	$-9 \le k \le 8$
		$-8 \le l \le 8$	$-9 \le l \le 11$
No. of reflections; R_{int}		3021; 0.0557	2181; 0.1035
No. of independent reflections		391	294
No. of obs. reflections $I > 2\sigma(I)$		343	250
No. of parameters		26	13
Space group; Z		*Pmma* (no. 51), 6	*P4/mnc* (no. 128), 2
Cell parameters	a [Å]	10.806(2)	5.878(2)
	b [Å]	3.1955(7)	–
	c [Å]	6.312(2)	6.857(2)
	V [Å^3]	217.96(8)	236.9(1)
Calculated density [g cm^{-3}]		13.39	8.04
Absorption coefficient μ [mm^{-1}]		84.914	72.619
Absorption correction		Semi-empirical	Semi-empirical
GooF		1.109	1.068
R_1; wR_2 (all I)		0.0301; 0.0463	0.0505; 0.0856
Difference peak/hole [e Å^{-3}]		−3.616/2.823	−5.900/5.078
ICSD-number[a]		429116	429117

[a] Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666; e-mail: crysdata@fiz-karlsruhe.de).

2.4. Magnetic measurements

In order to check for superconducting behavior, temperature-dependent susceptibility data for polycrystalline Ta_2OsB_2 and TaRuB samples were performed with a SQUID magnetometer (MPMS-5S, Quantum Design) in the temperature range 2–100 K at applied field $B_0 = 0.01$ T. The data were corrected for the sample holder (Teflon® tubes).

2.5. Electronic structure calculations

The ab-initio total energy and molecular dynamics program "Vienna *Ab-initio* Simulation Package" (VASP) [23] was used for structural optimization of TaRuB with the projector-augmented wave (PAW) method [24]. Exchange and correlation in this density functional theory (DFT)-based method were treated with the generalized gradient approximation (GGA) functional as parameterized by Perdew, Burke and Ernzerhof (GGA-PBE) [25] using an energy cut-off of 500 eV for the plane waves. The experimental lattice parameters were used as starting point of our calculations. Cell shape and volume variation were allowed during the structural optimization until a total energy self-consistency of 10^{-8} eV and until the self-consistency for the ionic relaxation of 10^{-6} eV. The k-mesh was chosen to be $5 \times 21 \times 11$ for TaRuB, and the algorithm by Monkhorst and Pack [26] was used. For details about the structural relaxation of Ta_2OsB_2 see reference [11].

Chemical bonding analyses were carried out on the most stable energy ground-state structure obtained from the VASP calculations of TaRuB, using the tight-binding, linear muffin-tin orbitals with the atomic spheres approximation (TB-LMTO-ASA) [27,28] as implemented in the TB-LMTO 4.7 program. Exchange and correlation were treated with the GGA-PW91 functional by Perdew et al. [29], a functional very similar to the GGA-PBE. The k-mesh was chosen to be $9 \times 29 \times 15$. The bonding analysis was done by calculation of the density-of-states (DOS), the crystal orbital Hamilton population (COHP) [30] and its integrals (ICOHP). The ICOHP can be seen as a semi-quantitative bonding energy which measures covalent contributions in solids. The Fermi level (E_F) was