Preparation and Bonding Peculiarities of Ternary Boron Compounds with Magnesium and Rhodium

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In spite of the numerous known ternary borides of platinum metals, especially with rare-earth metals, ternary borides of platinum metals with alkaline-earth metals were not systematically studied. Concerning the systems Mg–M–B, where M = platinum metal, only few ternary compounds were reported [1-4]. However, our investigation of the Mg–Rh–B system revealed that several ternary compounds are formed in several composition regions. In addition, these compounds are very peculiar objects from the viewpoint of chemical bonding character. In contrast to many other classes of inorganic compounds (e.g. oxides, fluorides, sulfides) the bonding in borides (i.e. nature of chemical bonding, formal electron balance, etc.) requires characterization. In magnesium rhodium ternary borides the composition variety leads to the realization of the different types of chemical bonding: from a metal-like cationic sublattice with embedded isolated RhB-anion units to a covalently bonded boron framework.

The pronounced difference in the reactivity of the initial reagents (Mg powder and Rh powder metals, crystalline boron) caused a number of problems in synthesis which were partly solved by using sealed tantalum ampoules as reactors, fine fraction (< 25 μm) of the crystalline boron or RhB precursor, and long (7–20 days) annealing at high temperatures (850–1250 °C) with intermediate regrinding. To avoid oxygen contamination of the samples, all preliminary synthetic operations were performed in an Ar-filled glove box.

The observed variety of the structure types requires to include a chemical bonding investigation into the studies. The chemical bonding situation was scrutinized using the Electron Localization Function, ELF [5-6].

The ternary compound Mg₆Rh₄B [7] exists in the metal-rich part of the Mg–Rh–B system. The crystal structure of Mg₆Rh₄B (space group Fdβm, a = 12.1711(4) Å, Z = 8, 174 reflections, R_f = 0.016) belongs to the filled Ti₂Ni structure type [8] and represents the first example of the Ti₂Ni structure motif stabilized by boron incorporation into the tetrahedral holes. From the geometrical point of view the Mg₆Rh₄B structure can be described as two interpenetrating frameworks formed by octahedra and tetrahedra (Fig. 1a). The octahedral framework is formed by two types of (Mg₁₆ octa-
hedra (Fig. 1b), and the tetrahedral framework consists of the Rh₄(Mg₂)₄ stellae quadrangula (Fig. 1c). The Rh₄ tetrahedra are centered by boron atoms ($d$(Rh–B) = 2.0073(3) Å), while each tetrahedral face is capped by the Mg₂ atom, forming the second coordination sphere around the boron atoms – the regular (Mg₂)₄ tetrahedra ($d$(Mg₂–B) = 2.6350(4) Å, $d$(Mg₂–Rh) = 2.7287(3) Å).

The topological description of the crystal structure of Mg₈Rh₄B as a filled variant of the Ti₂Ni structure motif suggests a rather weak interaction of the implemented boron atoms with the metallic matrix. Despite this implication, but in agreement with the fact that the binary Mg₈Rh₄ phase does not exist without boron, the ELF calculation reveals a strong covalent interaction within the (Mg₂)₄Rh₄B stellae quadrangula. The maxima of ELF are located on the four Rh–B bonds (Fig. 2a). The basins of these attractors form the valence shell of the boron atoms, and integration of the electron density results in 5.92 electrons. For the inner shells of the rhodium atoms, integration gives 44.88 = 45 electrons, and for the inner shells of the boron atoms 2.1 electrons. In total this leads to a rhodium-boron anion [Rh₄B]³⁻. Since the inner shells of the both types of Mg atoms contain = 10 electrons each, the total charge balance can be written as [Mg²⁺]₈[Rh₄B]³⁻·13e⁻. These results are in good agreement with the physical properties of Mg₈Rh₄B. The material is a good metallic conductor and reveals Pauli paramagnetic behaviour.

According to this bonding picture, the whole crystal structure, which by intuition should be rather metal-like, has to be understood as composed of two parts: covalently bonded polyanions [Rh₄B]³⁻ embedded in a cationic magnesium matrix (Fig. 2b). The unusually large number of excess electrons suggests additional (covalent) interactions within the magnesium matrix, which will be the subject of future studies.

An essential decrease of the metal/boron ratio leads to a condensation of isolated [RhₓBᵧ]⁻ anions to a two-dimensional (2D) polyanion [RhB] in the equiatomic compound Mg₁−xRhB [9]. The crystal structure (space group $P\overline{6}22$, $a$ = 5.2394(1) Å, $c$ = 9.4251(3) Å, $Z$ = 6, 228 reflections, $R(F)$ = 0.025) is presented in Fig. 3a. It shows a topological resemblance to the well-known CeCo₃B₂ structure type [10] (Fig. 3b). Along the [001] direction, the Mg₁−xRhB structure can be described as a sequence of six (Mg₁)B₂ and (Mg₂)Rh₂ layers alternating along the $c$ axis of the hexagonal unit cell (Fig. 3c). The (Mg₁)B₂ layers are similar to the CeB₂ layers in the CeCo₃B₂ structure, but in contrast to these the boron atoms in the (Mg₁)B₂ layers of the Mg₁−xRhB structure are shifted away from the (more symmetrical) positions on the three-fold axis. This displacement results in two short (2.777(6) Å) and one long (3.618(6) Å) Mg₁–B distances and leads to the formation of B–B contacts with a bond length of 1.840(8) Å. Compared to the flat Co₃ layers in the CeCo₃B₂ structure, the magnesium and rhodium atoms occupy similar positions in Mg₁−xRhB in an ordered manner giving rise to (Mg₂)Rh₂ layers, which are significantly puckered (Fig. 3c). Stacking of the (Mg₂)Rh₂ layers creates distorted trigonal prisms with 2 Mg₂ and 4 Rh atoms at the vertices.
Each prism is filled by a B atom with $d(\text{Rh–B}) = 2.189(5)$ Å, 2.220(3) Å and $d(\text{Mg2–B}) = 2.450(4)$ Å.

The crystal structure refinement revealed partial occupancy of the Mg1 site (0.95(1)), which is in accordance with results of the EDX measurements. The investigation of the homogeneity range $\text{Mg}_{1-x}\text{RhB}$ for $0.05 \leq x \leq 0.8$, showed that the decrease of the magnesium content is accompanied by a contraction of the $c$ parameter, while the $a$ parameter remains nearly unchanged.

The ELF shows two different attractor types in the valence region close to the boron and rhodium atoms: on the B–B contacts (3.0 e⁻ per bond) and on the shorter Rh–B contacts (2.6 e⁻ per bond) (Fig. 4a). The structuring in the outer core shell of rhodium suggests a participation of the 4$d$ states of rhodium in the bonding. The calculation of the atomic charges within the polyanion applying homolytic cleavage gives $\text{B}^{1.2–}$ and $\text{Rh}^{0.6–}$, thus suggesting only partial charge transfer from Mg sublattice to [RhB] polyanion: $\text{Mg}^{1.8+}[\text{Rh}^{0.6–}\text{B}^{1.2–}]$. This finding correlates with the observed deficiency in the cation positions within the homogeneity range of $\text{Mg}_{1-x}\text{RhB}$ and the change of the structural parameters with composition: the $c$ parameter, which corresponds to the Mg1–Mg1 distance, decreases with increasing $x$, while the $a$ parameter, determined by the rigid bonds inside the [RhB] polyanion, remains unchanged. Thus, the compound $\text{Mg}_{1-x}\text{RhB}$ represents the class of boridometallides, containing a 2D [RhB] polyanion.
with embedded magnesium cations (Fig. 4b). The material is a weakly diamagnetic, and the electrical resistivity shows a typical metallic temperature dependence being in good agreement with the results of the electronic structure calculation and the chemical bonding analysis.

Further decrease of the metal/boron ratio leads to dramatic changes of the bonding character in boron-rich ternary magnesium rhodium borides which can be illustrated by the rather peculiar structure of the novel compound Mg₅Rh₁₋ₓB₆₋₂ₓ[11] crystallizing in a modified Y₂ReB₆ structure type [12]. The crystal structure was determined using X-ray single crystal diffraction data of specimen with composition Mg₅Rh₀.₇₅B₆.₅ (space group Pham, a = 8.795(2) Å, b = 11.060(2) Å, c = 3.5279(5) Å, Z = 4, 630 reflections, R_f = 0.045) as confirmed by EDXS measurements. While isolated boron atoms exist in the metal-rich structure Mg₈Rh₄B and boron pairs in the equiatomic structure Mg₁₋ₓRhₓB, a three-dimensional (3D) boron framework is formed in the Mg₂Rh₁₋ₓB₆₋₂ₓ structure. In contrast to the well-known Y₂ReB₆ structure, consisting of planar boron nets and distorted close-packed layers of metal atoms, the Mg₂Rh₁₋ₓB₆₋₂ₓ structure is characterized by an alternating occupation of the 4g position by rhodium atoms (occupancy 0.75(1)) or by a boron pair (occupancy 0.25(1)). The boron dumbbell is oriented parallel to the c-axis with the center placed at the Rh atom position (Fig. 5a). The B–B interatomic distance within the pair is 1.77(4) Å and the distances between atoms of the pairs and boron atoms belonging to the neighboring planar boron nets are about 1.74(3) Å (1.71(3) ± 1.78(3) Å). Therefore, in case of the occupancy of the 4g position by the Rh atom, the crystal structure of Mg₅Rh₀.₇₅B₆.₅ is similar to the Y₂ReB₆ structure (Fig. 5b). The boron pairs link the nets to a 3D boron framework (Fig. 5c), containing pentagonal pyramidal units B₂ with very similar interatomic B–B distances. The rhodium/boron pair substitution leads to the existence of the homogeneity range Mg₂Rh₁₋ₓB₆₋₂ₓ in which the decrease of the rhodium content is accompanied by the reduction of the a and b parameters and the extension of the c parameter.

The Mg₅Rh₁₋ₓB₆₋₂ₓ is a very unusual modification of the Y₂ReB₆ type structure. For the analysis of the chemical bonding two models were investigated: Mg₅Rh₈B₆ with unmodified Y₂ReB₆ structure (space group Pham) and Mg₉Rh₀.₅B₂, with an ordered substitution of half of the rhodium atoms by boron dumbbells (space group P2₁/am). The ELF distribution of both models has similar main features. The structures comprise planar boron nets with strong covalent boron-boron interaction, while no directed bonds for Mg and Rh atoms (Fig. 6a, b) are observed. Integration of the electron density within ELF basins revealed the charges 2+ for Mg and Rh atoms. The unusual valence state of the Rh atom is

![Fig. 5: Crystal structure of Mg₂Rh₀.₇₅B₆.₅: (a) alternation of the atomic layers perpendicular to [001] in the structure of Mg₂Rh₀.₇₅B₆.₅; (b) [001] projection of the Mg₂Rh₈ structure with full occupancy of the 4g position by Rh atom; (c) 3D boron framework formed by stacking of the boron planes, containing the B₁–B₆ atoms, due to the boron pairs (B₇).](image)
confirmed by the deformation of the spherical outer core shell of Rh observed for both structures. In case of Mg2RhB6, the boron net is formed only by three-bonded boron atoms and the average value of the electron count is 2.67 e− per B–B bond for the whole net (Fig. 6c). The charge of boron atoms varies in the range from −0.94 to −1.15 with an average value of −1.02. Finally, the formal electron balance can be written as \([\text{Mg}^{2+}]_2[\text{Rh}^{2+}]_2[\text{B}^{−6}]_6\). This suggests that for the formation of the planar boron nets the transfer of 6 electrons per formula unit from the metal atoms to the boron polyanion is necessary.

The appearance of boron pairs in the Mg2Rh0.5B7 structure and, hence, the formation of a 3D boron framework leads to five-bonded (B(5b)) and six-bonded (B(6b)) boron atoms. A quantitative analysis of the chemical bonding shows that the electron count for bonds between three-bonded boron atoms has an average value of 2.69 e−, which is quite close to the situation in the non-modified Mg2RhB6 boron net (Fig. 6d, the boron positions splitted due to the symmetry reduction from \(P\text{bam}\) to \(P\text{2}_{1}\text{am}\) are marked as B(5b)). However, the appearance of boron pairs results in additional covalent bonds inside the B7 bipyramidal unit.

Fig. 6: ELF distributions, bond electron counts and atomic charges for the investigated compounds Mg2RhB6 and Mg2Rh0.5B6 (\(\eta = 0.75\) isosurface is shown). Interatomic distances are given for the nonequivalent B–B contacts: (a) ELF distribution for Mg2RhB6; (b) ELF distribution for Mg2Rh0.5B7; (c) electron counts for the planar boron net in Mg2RhB6; (d) electron counts for the planar boron net in Mg2Rh0.5B7; (e) electron counts for B–B bonds between B7–B7 atoms in the boron pair and inside the B7 bipyramidal unit.
bipyramidal units with much smaller electron count. The electron count for B(5b)–B(5b) bonds inside the pentagonal ring has an average value of 1.29 e\textsuperscript{−} per bond (Fig. 6e). Boron-boron interactions between boron atoms of the pair (B(6b)) and boron atoms belonging to the pentagonal ring (B(5b)) are characterized by even smaller electron counts with the average value of 0.73 e\textsuperscript{−}, whereas B(6b)–B(6b) bonds are simple two-electron bonds. The average charges are −1.10 for three-bonded boron atoms, −0.44 for five-bonded boron atoms and +0.08 for six-bonded boron atoms. These data allow to write the formal electron balance as:

\[
[Mg^{2+}]_2[Rh^{2+}]_{0.5}[B(3b)^{1.1–}]_{3.5}[B(5b)^{0.44}]_{2.5}
\]

\[
[B(6b)^{0.08–}]_{1.1–}[Mg^{2+}]_2[Rh^{2+}]_{0.5}[B_7]_{5.03–}.
\]

The chemical bonding analysis revealed that with the appearance of the boron dumbbells at half of the rhodium positions and, hence, with the formation of a 3D boron framework, the charge redistribution takes place within the boron framework. The electron charge transfer per metal atom does not change so that the scheme of the electron transfer from the metal atoms to the boron sublattice remains conserved. Consequently, the boron dumbbells replacement in the Y\textsubscript{2}ReB\textsubscript{6} structure motif compensates the electron deficiency, caused by rhodium vacancies. From this point of view, a homogeneity area is expected to exist for the compound Mg\textsubscript{2}Rh\textsubscript{1−x}B\textsubscript{6+2x}, a prediction which is supported by experimental results.

A polycrystalline sample of Mg\textsubscript{2}Rh\textsubscript{1−x}B\textsubscript{6+2x} with x = 0.4 shows diamagnetic behavior, while the electrical resistivity of the compound is high and varies only little with temperature. The magnitude and the temperature dependence of \(\rho(T)\) are reminiscent of a system close to a continuous metal-insulator transition.

Consequently, in spite of the approximately equal electronegativities of Rh and B, and the fact, that both are much more electronegative as magnesium, among the compounds in the ternary system Mg–Rh–B we observe different bonding situations depending on the composition. In the equiatomic compound Mg\textsubscript{1.5}RhB rhodium together with boron form a 2D polyanion. An increase of magnesium and rhodium content in Mg\textsubscript{4}Rh\textsubscript{1}B does not change the covalent Rh–B interaction, but reduces the dimensionality of the anionic part to the isolated [Rh\textsubscript{2}B\textsubscript{5}]\textsuperscript{−} anions. At high boron content, in Mg\textsubscript{2}Rh\textsubscript{1−x}B\textsubscript{6+2x} both rhodium and magnesium, act as a cationic counterpart for a 3D boron polyanion.

References


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