

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 Mg₈Rh₄B [7] exists in the metal-rich part of the Mg–Rh–B system. The crystal structure of Mg₈Rh₄B (space group $Fd\bar{3}m$, $a = 12.1711(4)$ 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 Mg₈Rh₄B structure can be described as two interpenetrating frameworks formed by octahedra and tetrahedra (Fig. 1a). The octahedral framework is formed by two types of (Mg1)₆ octa-

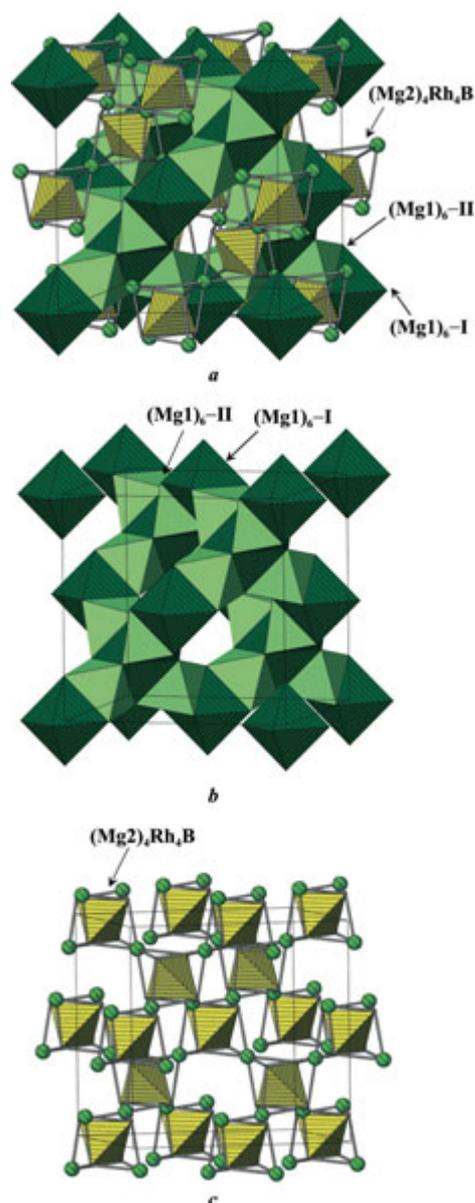


Fig 1: Crystal structure of Mg₈Rh₄B: (a) interpenetration of the tetrahedral and octahedral frameworks; (b) framework formed by face-sharing (Mg1)₆-I and (Mg1)₆-II octahedra; (c) framework of the stellae quadrangula (Mg₂)₄Rh₄B.

hedra (Fig. 1b), and the tetrahedral framework consists of the $\text{Rh}_4(\text{Mg}2)_4$ *stellae quadrangula* (Fig. 1c). The Rh_4 tetrahedra are centered by boron atoms ($d(\text{Rh}-\text{B}) = 2.0073(3)$ Å), while each tetrahedral face is capped by the Mg2 atom, forming the second coordination sphere around the boron atoms – the regular $(\text{Mg}2)_4$ tetrahedra ($d(\text{Mg}2-\text{B}) = 2.6350(4)$ Å, $d(\text{Mg}2-\text{Rh}) = 2.7287(3)$ Å).

The topological description of the crystal structure of $\text{Mg}_8\text{Rh}_4\text{B}$ as a filled variant of the Ti_2Ni 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 Mg_8Rh_4 phase does not exist without boron, the ELF calculation reveals a strong covalent interaction within the $(\text{Mg}2)_4\text{Rh}_4\text{B}$

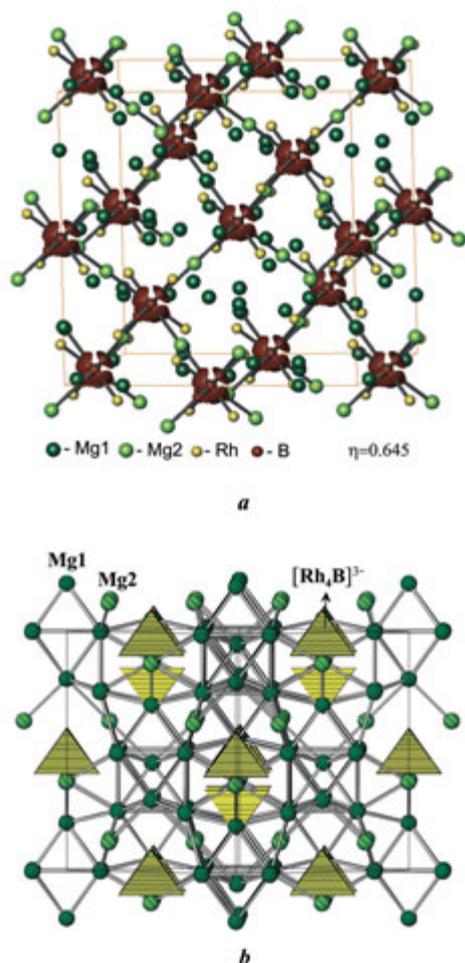


Fig. 2: Chemical bonding in $\text{Mg}_8\text{Rh}_4\text{B}$: (a) electron localization function for $\text{Mg}_8\text{Rh}_4\text{B}$: isosurfaces $\eta = 0.645$ revealing B–Rh bonds within the stellae quadrangula; (b) covalently bonded polyanions $[\text{Rh}_4\text{B}]^{3-}$ embedded in a cationic matrix in the crystal structure of $\text{Mg}_8\text{Rh}_4\text{B}$.

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 $44.88 \approx 45$ electrons, and for the inner shells of the boron atoms 2.1 electrons. In total this leads to a rhodium-boron anion $[\text{Rh}_4\text{B}]^{3-}$. Since the inner shells of the both types of Mg atoms contain ≈ 10 electrons each, the total charge balance can be written as $[\text{Mg}^{2+}]_8[\text{Rh}_4\text{B}]^{3-} \cdot 13e^-$. These results are in good agreement with the physical properties of $\text{Mg}_8\text{Rh}_4\text{B}$. 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 $[\text{Rh}_4\text{B}]^{3-}$ 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 $[\text{Rh}_x\text{B}_y]^{z-}$ anions to a two-dimensional (2D) polyanion $[\text{RhB}]$ in the equiatomic compound $\text{Mg}_{1-x}\text{RhB}$ [9]. The crystal structure (space group $P6_222$, $a = 5.2394(1)$ 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 CeCo_3B_2 structure type [10] (Fig. 3b). Along the $[001]$ direction, the $\text{Mg}_{1-x}\text{RhB}$ structure can be described as a sequence of six $(\text{Mg}1)\text{B}_2$ and $(\text{Mg}2)\text{Rh}_2$ layers alternating along the c axis of the hexagonal unit cell (Fig. 3c). The $(\text{Mg}1)\text{B}_2$ layers are similar to the CeB_2 layers in the CeCo_3B_2 structure, but in contrast to these the boron atoms in the $(\text{Mg}1)\text{B}_2$ layers of the $\text{Mg}_{1-x}\text{RhB}$ 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 Co_3 layers in the CeCo_3B_2 structure, the magnesium and rhodium atoms occupy similar positions in $\text{Mg}_{1-x}\text{RhB}$ in an ordered manner giving rise to $(\text{Mg}2)\text{Rh}_2$ layers, which are significantly puckered (Fig. 3c). Stacking of the $(\text{Mg}2)\text{Rh}_2$ layers creates distorted trigonal prisms with 2 Mg2 and 4 Rh atoms at the vertices.

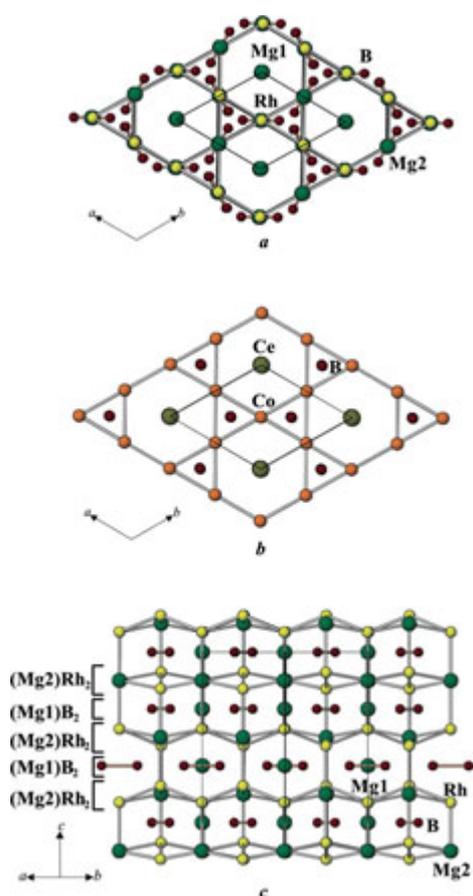


Fig. 3: Crystal structures of $Mg_{1-x}RhB$ and $CeCo_3B_2$: (a) [001] projection of the $Mg_{1-x}RhB$ structure; (b) [001] projection of the $CeCo_3B_2$ structure; (c) stacking of the atomic layers perpendicular to [001] in the structure of $Mg_{1-x}RhB$.

Each prism is filled by a B atom with $d(Rh-B) = 2.189(5) \text{ \AA}$, $2.220(3) \text{ \AA}$ and $d(Mg2-B) = 2.450(4) \text{ \AA}$. 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 $Mg_{1-x}RhB$ 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 $4d$ states of rhodium in the bonding. The calculation of the atomic charges within the polyanion applying homolytic cleavage gives $B^{1.2-}$ and $Rh^{0.6-}$, thus sug-

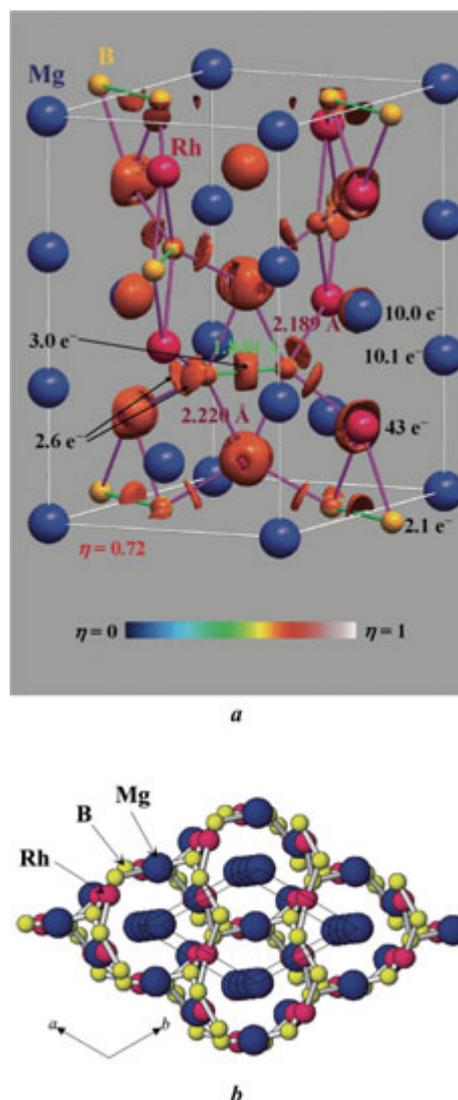


Fig. 4: Chemical bonding in $Mg_{1-x}RhB$: (a) isosurface of the electron localization function with $\eta = 0.72$ (orange). Interatomic distances are given for the short contacts in the rhodium-boron polyanion; (b) the crystal structure of $Mg_{1-x}RhB$ from the ELF representation as a two-dimensional [RhB] polyanion and the embedded Mg cations.

gesting only partial charge transfer from Mg sublattice to [RhB] polyanion: $Mg^{1.8+}[Rh^{0.6-}B^{1.2-}]$. This finding correlates with the observed deficiency in the cation positions within the homogeneity range of $Mg_{1-x}RhB$ 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 $Mg_{1-x}RhB$ 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 $\text{Mg}_2\text{Rh}_{1-x}\text{B}_{6+2x}$ [11] crystallizing in a modified Y_2ReB_6 structure type [12]. The crystal structure was determined using X-ray single crystal diffraction data of specimen with composition $\text{Mg}_2\text{Rh}_{0.75}\text{B}_{6.5}$ (space group $Pbam$, $a = 8.795(2)$ 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 $\text{Mg}_8\text{Rh}_4\text{B}$ and boron pairs in the equiatomic structure $\text{Mg}_{1-x}\text{RhB}$, a three-dimensional (3D) boron framework is formed in the $\text{Mg}_2\text{Rh}_{1-x}\text{B}_{6+2x}$ structure. In contrast to the well-known Y_2ReB_6 structure, consisting of planar boron nets and distorted close-packed layers of metal atoms, the $\text{Mg}_2\text{Rh}_{1-x}\text{B}_{6+2x}$ 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 $\text{Mg}_2\text{Rh}_{0.75}\text{B}_{6.5}$ is similar to the Y_2ReB_6 structure (Fig. 5b). The boron pairs link the nets to a 3D boron framework (Fig. 5c), containing pentagonal pyramidal units B_7 with very similar interatomic B–B distances. The rhodium/boron pair substitution leads to the existence of the homogeneity range $\text{Mg}_2\text{Rh}_{1-x}\text{B}_{6+2x}$ 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 $\text{Mg}_2\text{Rh}_{1-x}\text{B}_{6+2x}$ is a very unusual modification of the Y_2ReB_6 type structure. For the analysis of the chemical bonding two models were investigated: Mg_2RhB_6 with unmodified Y_2ReB_6 structure (space group $Pbam$) and $\text{Mg}_2\text{Rh}_{0.5}\text{B}_7$ with an ordered sub-

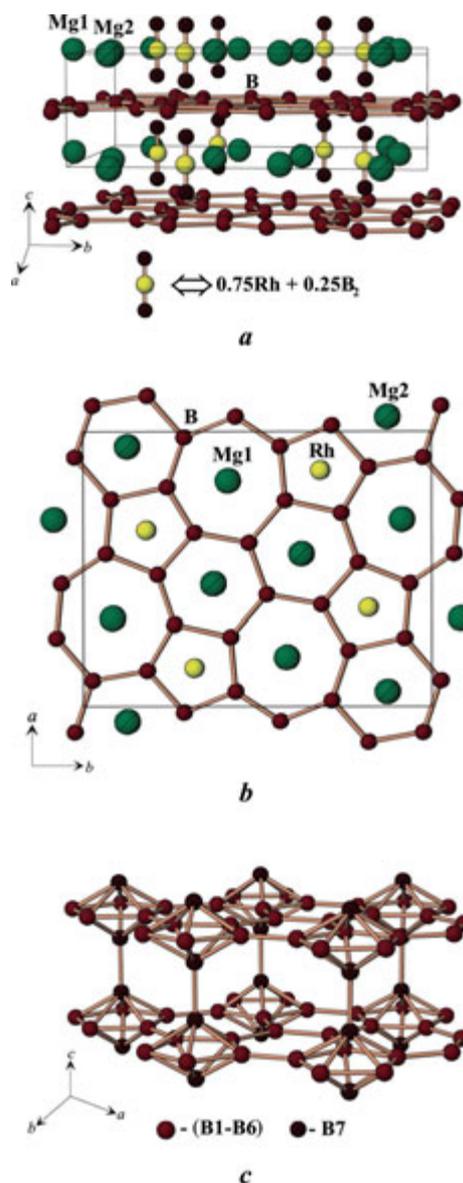
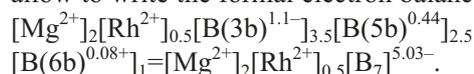


Fig. 5: Crystal structure of $\text{Mg}_2\text{Rh}_{0.75}\text{B}_{6.5}$:
 (a) alternation of the atomic layers perpendicular to $[001]$ in the structure of $\text{Mg}_2\text{Rh}_{0.75}\text{B}_{6.5}$;
 (b) $[001]$ projection of the Mg_2RhB_6 structure with full occupancy of the 4g position by Rh atom;
 (c) 3D boron framework formed by stacking of the boron planes, containing the B1–B6 atoms, due to the boron pairs (B_7)₂.

stitution of half of the rhodium atoms by boron dumbbells (space group $P2_1am$). 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

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 $1.29 e^-$ 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 $0.73 e^-$, 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:



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_2ReB_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 $\text{Mg}_2\text{Rh}_{1-x}\text{B}_{6+2x}$, a prediction which is supported by experimental results.

A polycrystalline sample of $\text{Mg}_2\text{Rh}_{1-x}\text{B}_{6+2x}$ 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 $\text{Mg}_{1-x}\text{RhB}$ rhodium together with boron form a 2D polyanion. An increase of magnesium and rhodium content in $\text{Mg}_8\text{Rh}_4\text{B}$ does not change the covalent Rh–B interaction, but reduces the dimensionality of the anionic part to the isolated $[\text{Rh}_4\text{B}]^{3-}$ anions. At high boron content, in $\text{Mg}_2\text{Rh}_{1-x}\text{B}_{6+2x}$, both rhodium and magnesium, act as a cationic counterpart for a 3D boron polyanion.

References

- [1] *W. Jung, B. Schmidt, Z. Anorg. Allg. Chem.* **543** (1986) 89.
- [2] *K. Schweitzer, W. Jung, Z. Anorg. Allg. Chem.* **530** (1985) 127.
- [3] *J. Schiffer, W. Jung, J. Solid State Chem.* **154** (2000) 232.
- [4] *W. Jung, J. Schiffer, Z. Anorg. Allg. Chem.* **581** (1990) 135.
- [5] *A. D. Becke, K. E. Edgecombe, J. Chem. Phys.* **92** (1990) 5397.
- [6] *M. Kohout, K. Perual, F. R. Wagner, Yu. Grin, Theor. Chem. Acc.* **112** (2004) 453.
- [7] *A. M. Alekseeva, A. M. Abakumov, A. Leithe-Jasper, W. Schnelle, Yu. Prots, P. S. Chizhov, G. Van Tendeloo, E. V. Antipov, Yu. Grin, Submitted to J. Solid State Chem.* (2005).
- [8] *G. A. Yurko, J. W. Barton, J. Gordon Parr, Acta Crystallogr.* **12** (1959) 909.
- [9] *A. M. Alekseeva, A. M. Abakumov, A. Leithe-Jasper, W. Schnelle, Yu. Prots, J. Hadermann, G. Van Tendeloo, E. V. Antipov, Yu. Grin, Z. Anorg. Allgem. Chem.* **631** (2005) 1047.
- [10] *Yu. Kuz'ma, P. Kripyakevich, N. S. Bilonizhko, Dopov. Akad. Nauk Ukr. RSR, Ser. A* (1969) 939.
- [11] *A. M. Alekseeva, A. M. Abakumov, P. S. Chizhov, A. Leithe-Jasper, W. Schnelle, Yu. Prots, G. Van Tendeloo, E. V. Antipov, Yu. Grin, Submitted to Inorg. Chem.* (2005).
- [12] *Yu. B. Kuz'ma, S. I. Svarichevskaya, Sov. Phys. Crystallogr. (Eng. Trans.)* **17(3)** (1972) 569.

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