

MS15-P20 Theoretical analysis of MB_2 , M_3B_4 and M_5B_6 ($M=V, Nb, Ta, Cr$). Vanessa Sagawe,^a Harald Hillebrecht,^a
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The AlB_2 structure-type consists of layers of B_6 -rings and a metal atom located in the hexagonal prismatic voids. With the increase of the ratio of $M:B$, the B_6 -rings form chains (M_3B_4) and chains of single B-atoms besides B_6 -chains (M_5B_6). Besides the metal atoms in the hexagonal prismatic voids, there are interstitial metal atoms. Kiessling [1] first investigated the crystal structure of Ta_3B_4 and found very different distances in the B_6 -ring-chains. One bond was very short (1.57 Å), the other remarkably long (1.85 Å). Hoffmann et al. [2] investigated this structure by Extended Hückel calculations. They tried to find out why the distances in Ta_3B_4 are so different from the ones found in MB_2 and M_5B_6 . In order to get information on the bonding situation in these three types of transition metal borides, we performed DFT-LAPW-calculations and we also optimized the geometry. This optimization resulted in very similar structures for all M_3B_4 with similar distances between all atoms of the B_6 -ring. So the structure found by Kiessling could not be verified. Maybe his results were biased because of the high absorption coefficient of Ta_3B_4 . The optimized and the not optimized structures were examined by QTAIM-Analysis as introduced by Bader [3]. The bonding between the M-atoms and the B-atoms are clearly ionic. The M in the hexagonal prismatic voids is more positive charged than the other ones in the structure. Also with increasing atomic number, the metal atoms in the structures become more positive charged. There is a small difference in the negative charge of the two different B-atoms of the B_6 -ring-chain. The density at the bond critical points in the B_6 -ring-chain in M_5B_6 is a bit smaller than in the other structures.

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MS15-P21 Experimental and theoretical Electron Density in MgB_7 . Vanessa Sagawe,^a Harald Hillebrecht,^a
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Bonding in Boron-rich borides is a challenging topic as one finds two types of bonds in these compounds [1]: Two-electron-two-centre-bonds and two-electron-three-centre-bonds. As these two types of bonds are also found in elemental boron, these systems may serve as model systems for elemental boron. Furthermore the investigated Boron-rich boride, MgB_7 [2,3], is very interesting as it contains a B_2 -unit with an unusual long distance of 2.27 Å. So studying the charge distribution of MgB_7 can verify whether there is a true bond between these two atoms or not. The structure consists of hexagonal primitive packed B_{12} -icosahedra. In the resulting trigonal prismatic voids there is alternating the B_2 -unit and a Mg-atom located. The charge distribution of MgB_7 was investigated by experimental electron density analysis. High resolution X-Ray single crystal diffraction data was analyzed by the program package XD2006 [4]. The results were analyzed by the QTAIM theory as introduced by Bader [5]. The bonding interaction inside the icosahedra is very different from the exohedral bonding. The density is delocalized over the whole surface of the icosahedron. A bond critical point (BCP) is found between all B of the icosahedron, the density at this point is about $0.7 \text{ e}/\text{Å}^3$ for all bonds. A ring critical point is found on every face. Between the two B-Atoms of the B_2 -unit a BCP could also be found. However the density at this point is about half ($0.45 \text{ e}/\text{Å}^3$) the density of the BCP in the other non-icosahedral bonds (0.9 and $0.8 \text{ e}/\text{Å}^3$). The interstitial B-atoms are the most negative Atoms of the structure (-0.5). These results could also be confirmed by theoretical DFT-LAPW-calculations.

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