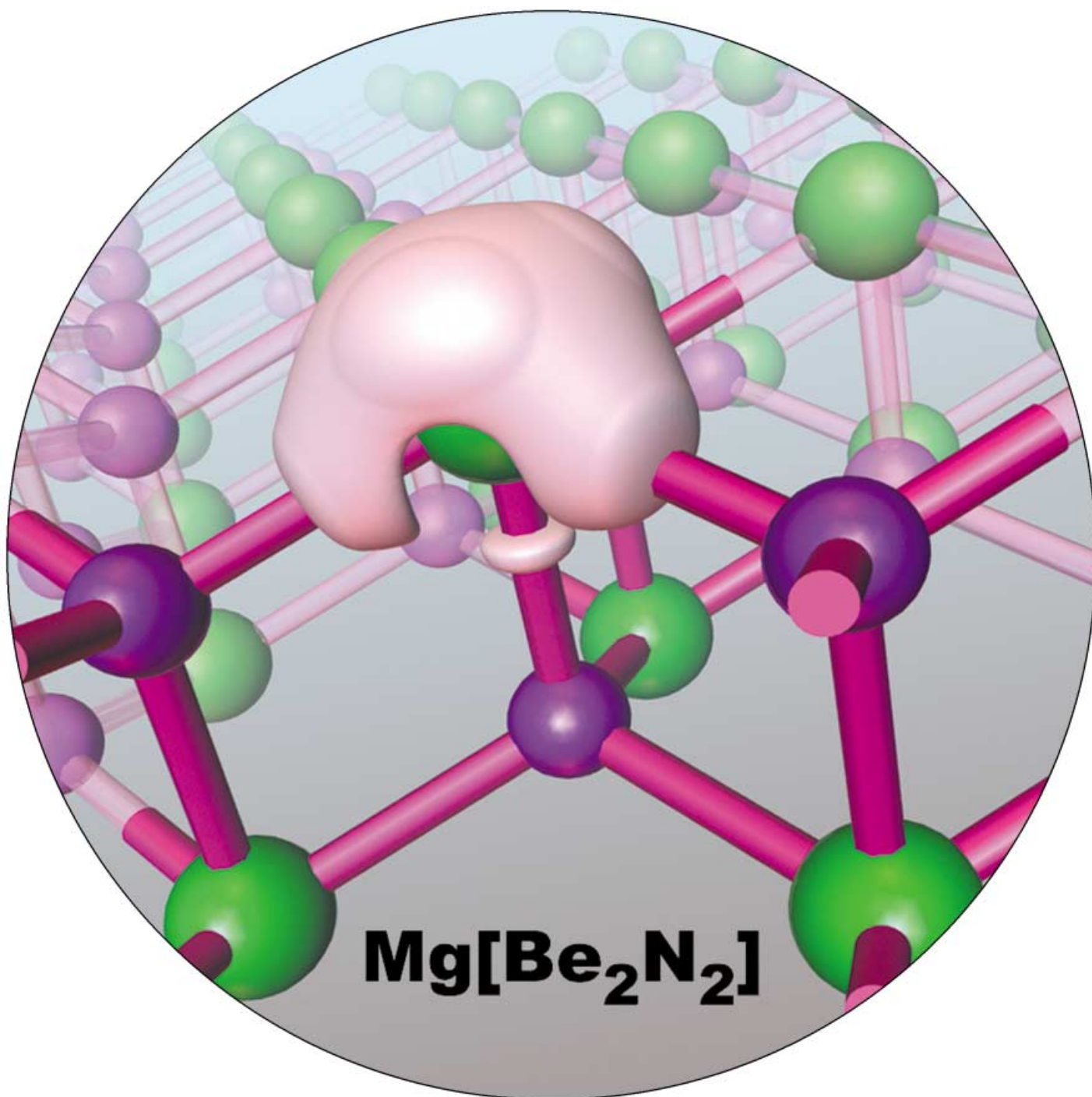


Communications



The nitridoberyllates of the heavier alkaline-earth metals contain anion layers with covalent Be–N bonds. Mg[Be₂N₂] occupies a special position among this class of compounds, since, unlike the Ca, Sr, and Ba compounds, it contains puckered [BeN] layers. For more information on these structures see the Communication by R. Kniep et al. on the following pages.

Layered Compounds

Ae[Be₂N₂]: Nitridoberyllates of the Heavier Alkaline-Earth Metals**

Mehmet Somer, Alper Yarasik, Lev Akselrud, Stefano Leoni, Helge Rosner, Walter Schnelle, and Rüdiger Kniep*

Dedicated to Professor Bernt Krebs on the occasion of his 65th birthday

The first and only known nitridoberyllate up to now, Li[BeN],^[1] was reported in 1996. The crystal structure contains puckered 4.8² nets in which Be and N alternate. Neighboring $\infty^2[(\text{Be}_{3/3}\text{N}_{3/3})^-]$ nets are connected through Li cations, which are tetrahedrally coordinated by nitrogen. Attempts to replace Li by the heavier and larger alkali metals Na or K, have not been successful. However, success could be achieved with the heavier homologues of beryllium. Compounds of the composition Ae[Be₂N₂] (Ae = Mg, Ca, Sr, Ba) were synthesized as microcrystalline powders.^[2] On the basis of the chemical formula alone, the compounds could be expected to crystallize as a substitutional variant of the polymorphic modifications of beryllium nitride: Be₃N₂ exists in a cubic low-temperature modification^[3,4] with the α -Mn₂O₃-type structure and beryllium tetrahedrally coordinated by nitrogen, as well as in a hexagonal high-temperature modification^[5,6] in which beryllium is coordinated in a tetrahedral and trigonal-planar fashion by nitrogen. Another likely structure could be the (anti-)La₂O₃-type structure,^[7] which is often found in ternary phases. The mixed alkaline-earth metal nitride CaMg₂N₂^[8] and the ternary nitrides Li₂ZrN₂^[9] and Li₂CeN₂^[10] also crystallize in this latter type.

The crystal structures^[11] of the novel compounds Ae[Be₂N₂] contain complex anion layers with covalent bonds between beryllium and nitrogen and are therefore characterized as nitridoberyllates. Mg[Be₂N₂] crystallizes in the above-mentioned La₂O₃-type structure,^[7] whereas the Ca, Sr, and Ba compounds are isostructural to the boride-carbide Ca[B₂C₂].^[12] The latter contains planar 4.8² layers of alternating boron and carbon atoms. The anionic partial structure [B₂C₂²⁻] is isoelectronic with [Be₂N₂²⁻] (16e⁻ systems).

Mg[Be₂N₂] contains puckered Be-N six-membered rings in chair conformation, which are condensed to single layers

parallel (001) and which are pairwise connected to form double layers along [001] (Figure 1). The stacking of the puckered double nets is such that Be and N alternate, as they do within a single net. Nitrogen occupies the positions at the

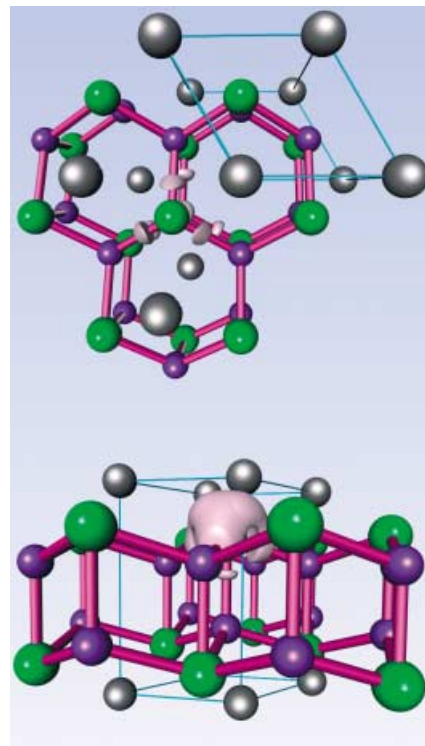


Figure 1. Crystal structure of Mg[Be₂N₂]. Mg: gray; Be: purple; N: green. Top: View along [001]. The electron localization function (ELF) ($\eta = 0.84$) shows localization domains between Be and N in the puckered 6² nets. Bottom: Skew view along [110]. The ELF ($\eta = 0.80$) shows a localization domain as a large maximum around N as well as a smaller axial localization domain.

outer boundaries of the double layers. Beryllium and nitrogen are surrounded by four nitrogen and four beryllium atoms, respectively, with distances $d(\text{Be-N}) = 178.4(4)$ pm ($3 \times$) and $176.0(1)$ pm. Beryllium is tetrahedrally coordinated by nitrogen, while nitrogen occupies the apex of a trigonal pyramid whose base is made of three Be positions (Be'). The fourth Be position (Be'') belongs to the adjacent net of the double layer and is placed therefore below the base of the trigonal pyramid. The resulting nitrogen coordination can be described as an inverse tetrahedron. The angle Be'-N-Be'' is $73.1(4)^\circ$, and the angle Be'-N-Be' is $111.9(3)^\circ$ and thus close to the value for a tetrahedral arrangement. Magnesium is placed between the complex double-layer anions $\infty^2[(\text{Be}_{3/3}\text{N}_{3/3})^{2-}]$ and is octahedrally surrounded by nitrogen ($d(\text{Mg-N}) = 220.9(2)$ pm).

Ca[Be₂N₂] and Sr[Be₂N₂] are isotypic. Analogously to Li[BeN],^[1] the crystal structure contains 4.8² nets $\infty^2[(\text{Be}_{3/3}\text{N}_{3/3})^{2-}]$ that are stacked along [001]. Unlike Li[BeN], the nets are not puckered but strictly planar. The (...AB...) stacking of the planar nets, which are slightly rotated with respect to each other, causes Be and N to alternate also along [001] (Figure 2). The octagonal prismatic voids between the

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[**] Ae = Mg, Ca, Sr, Ba. We gratefully acknowledge Dr. Wilder Carrillo-Cabrera for his support with the analysis of the X-ray powder data, and Prof. Dr. Matthias Driess for stimulating discussions.

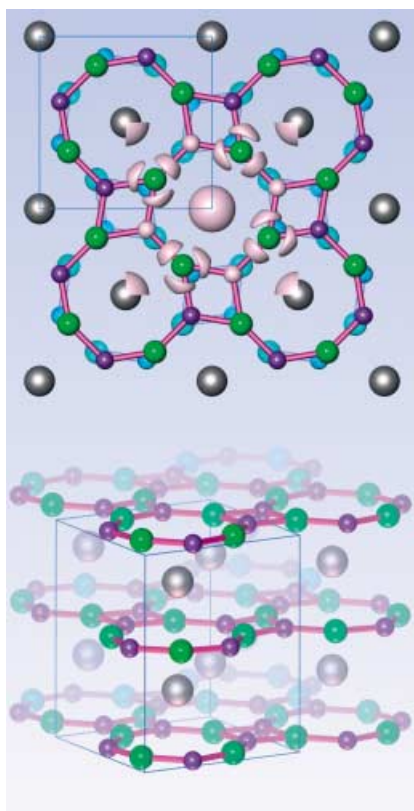


Figure 2. Crystal structure of $\text{Ca}[\text{Be}_2\text{N}_2]$. Ca: gray; Be: purple; N: green. Top: View along [001]. ELF localization domains ($\eta=0.81$) show up in the planar 4.8^2 net between Be and N. See text for details. The next lower lying layer is displayed in slightly different colors while preserving the atom sizes. Bottom: stacking of the layers along [001] and cations in between in the centers of the octagonal prisms.

nitridoberyllate layers are centered by charge-balancing Ca^{2+} or Sr^{2+} ions. The Be–N distances within the layers, of 163.2(6) pm ($2\times$) and 165.7(6) pm for the Ca compound, 163.0(2) pm ($2\times$) and 167.0(2) pm for the Sr compound, are clearly shorter than the ones in $\text{Mg}[\text{Be}_2\text{N}_2]$.

Planar 4.8^2 nets are also present in the anionic partial structure of the isotopic boride-carbide $\text{Ca}[\text{B}_2\text{C}_2]$.^[12] Here also the stacking sequence of the layers causes the nonmetal atoms in neighboring layers to alternate. The structurally closely related compound $\text{Ce}[\text{B}_2\text{C}_2]$ ^[13] shows the same stacking sequence, whereby the arrangement of the two kinds of atoms in neighboring anionic layers is congruent: boron is placed over boron, and carbon over carbon. The same congruent motif is also adopted by the lithium–nitrogen anionic partial structure in $\text{Ca}\{\text{Li}_2[\text{Mn}^{\text{I}}\text{N}_2]\}$.^[14] Here the 4.8^2 nets are additionally connected to each other by (N–Mn^I–N) groups, such that the Ca^{2+} ions abandon the octagonal prismatic voids to occupy the centers of the net octagons. The succession of Be and N along [001] in the crystal structure of $\text{Ca}[\text{Be}_2\text{N}_2]$ was checked with a full-potential calculation^[15] with the FPLO method (full potential minimum basis local orbital scheme).^[16] For this two ordering schemes (congruent and alternating sequence of the atom sorts along [001]) were defined in space group $P4/m3m$. The alternation of Be and N within the layers was preserved. With an energy gain of 0.6 eV

per Be–N bond the alternating sequence along [001] is clearly favored and confirms thereby the experimental finding. Unlike the significantly high gain in energy for the Be–N bond, the gain for the C–B bond in the isotopic compound $\text{Ca}[\text{B}_2\text{C}_2]$ ^[12] is more than one order of magnitude smaller. The still controversial discussion on the layer stacking in the boride-carbide compound can therefore be only partially clarified with ab initio calculations.^[17]

The magnetic susceptibilities $\chi(T) = M(T)/H$ of samples of the $Ae[\text{Be}_2\text{N}_2]$ compounds consist of a constant and a field- and temperature-dependent contribution. The latter can be explained by minor paramagnetic and ferromagnetic impurities. The corrected values for the susceptibility $\chi_{\text{corr}}(300\text{ K})$ amount to -28.5 ($\text{Mg}[\text{Be}_2\text{N}_2]$), -35.3 ($\text{Ca}[\text{Be}_2\text{N}_2]$), and $-60.3 \times 10^{-6} \text{ emu mol}^{-1}$ ($\text{Ba}[\text{Be}_2\text{N}_2]$). Using the diamagnetic increments $\chi_{\text{dia}}^{\text{[18]}}$ for the alkaline-earth ions Ae^{2+} a value of $\chi_{\text{A}}(300\text{ K}) = (-27 \pm 2) \times 10^{-6} \text{ emu mol}^{-1}$ can be calculated for the $[\text{Be}_2\text{N}_2]$ anion. The nitridoberyllates are therefore diamagnetic. In agreement with the electronic density of state no Pauli paramagnetism was detected. Phase transitions were also not observed.

The bonding situation in the compounds $\text{Mg}[\text{Be}_2\text{N}_2]$, $\text{Ca}[\text{Be}_2\text{N}_2]$, and $\text{Sr}[\text{Be}_2\text{N}_2]$ was analyzed by means of electron localization function (ELF) calculations.^[19–21] For $\text{Mg}[\text{Be}_2\text{N}_2]$ the ELF ($\eta=0.80$) shows a large valence basin around nitrogen and a smaller basin between Be and N along the geometric line parallel to the c axis (Figure 1 and 3). At $\eta =$

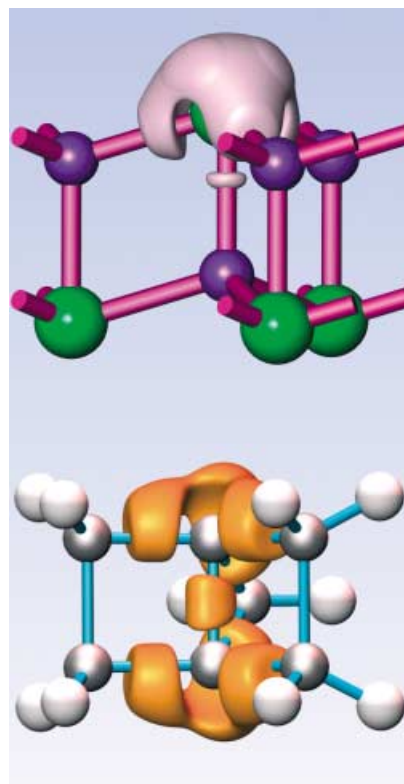


Figure 3. Comparison of ELF topologies. Top: Around nitrogen in $\text{Mg}[\text{Be}_2\text{N}_2]$ ($\eta=0.80$). Bottom: At a bridgehead carbon atom in [2.2.1]propellane ($\eta=0.73$). The ELF characteristics of such an inverse geometry consist of a large basin, which decays into three localization domains as well as a smaller axial basin. See text for details.

0.84 the valence basin around nitrogen decays into three equivalent localization domains between Be and N, corresponding to the bonds of the puckered 6^3 nets, while the small axial basin has disappeared (Figure 1). Upon integration of the electronic density in the ELF basins^[22] a value of 2.4 electrons per Be–N bond in the 6^3 nets is found. The smaller basin contains 0.8 electrons. The bonding situation of nitrogen is thus the one of an inverse tetrahedron and is reminiscent of the bridgehead carbon atoms in propellanes.^[23] ELF calculations of different propellanes with varying ring sizes ($[l.m.n]$ propellanes; $l,m,n=1,2$) show in each case a small basin between the bridgehead carbon atoms, and a large valence basin that decays into three localization domains.^[24] This situation is illustrated in Figure 3 for the example of the bridgehead carbon atoms in $[2.2.1]$ propellane. For the whole $[\text{Be}_2\text{N}_2]$ net in the crystal structure of $\text{Mg}[\text{Be}_2\text{N}_2]$ the integration over all bonding basins amounts to 1.93 electrons, which is in agreement with the description of the compound as a nitridoberyllate.

The ELF of the isotopic compounds $\text{Ca}[\text{Be}_2\text{N}_2]$ and $\text{Sr}[\text{Be}_2\text{N}_2]$ are topologically identical. For reasons of symmetry, within the planar 4.8^2 nets there are two different bonds. Accordingly, for $\eta=0.82$ the ELF shows two different localization domains (Figure 2). The eccentric position of one of the domains with respect to the geometric line between Be and N reflects the local strain caused by the four-membered ring. The bond that belongs to the eight-membered ring only is represented by a localization domain, which is found on the geometric bonding line. Both bonds correspond to 2.7 and 2.5 electrons, respectively (by integration of

the electronic density in the ELF basins^[22]). For the whole $[\text{Be}_2\text{N}_2]$ net an excess of 1.65 electrons (Ca compound) and 1.6 electrons (Sr compound), respectively, is found. This value, which clearly deviates from two electrons, together with the structuring of the Ca- and Sr-core basins at higher ELF values,^[25] is indicative of a participation of Ca and Sr d orbitals in the covalent chemical bonding. Accordingly, a Bader analysis^[26] of the electronic density yields values of $\text{Ca}^{1.4+}$ and $\text{Sr}^{1.4+}$.

Figure 4 shows the electronic structures (band structures and DOS)^[20] of $\text{Mg}[\text{Be}_2\text{N}_2]$ and $\text{Ca}[\text{Be}_2\text{N}_2]$ ($\text{Sr}[\text{Be}_2\text{N}_2]$). For $\text{Mg}[\text{Be}_2\text{N}_2]$ the region from -7 eV up to the Fermi level is dominated by nitrogen states. The quasi-two-dimensional character of the (Be–N)- $2p$ - σ bands is reflected in a small dispersion orthogonal to the hexagonal plane, and generates a large density of states below the Fermi level. No band crosses the Fermi level. At the Γ point a large band gap of about 4.5 eV is opened. This gap is caused by the heteropolar Be–N bonds within the Be–N layers (in analogy to the band gap in $\text{Li}[\text{BC}]$ with covalent bonds in the anionic partial structure).^[27] The bands above 4.5 eV are mainly characterized by Mg states. The DOS shows the large contribution of N p states close to the Fermi level. For $\text{Ca}[\text{Be}_2\text{N}_2]$ ($\text{Sr}[\text{Be}_2\text{N}_2]$) the region from -5.0 eV up to the Fermi level is also dominated by N states. Like in $\text{Mg}[\text{Be}_2\text{N}_2]$, the quasi-two-dimensional character of some bands brings a considerable density of states just below the Fermi level, which is again not crossed by any band. At the Γ point a direct band gap of approximately 1.8 eV (1.4 eV) is opened. The bands above 1.8 eV (1.4 eV) show Ca and Sr character, respectively.

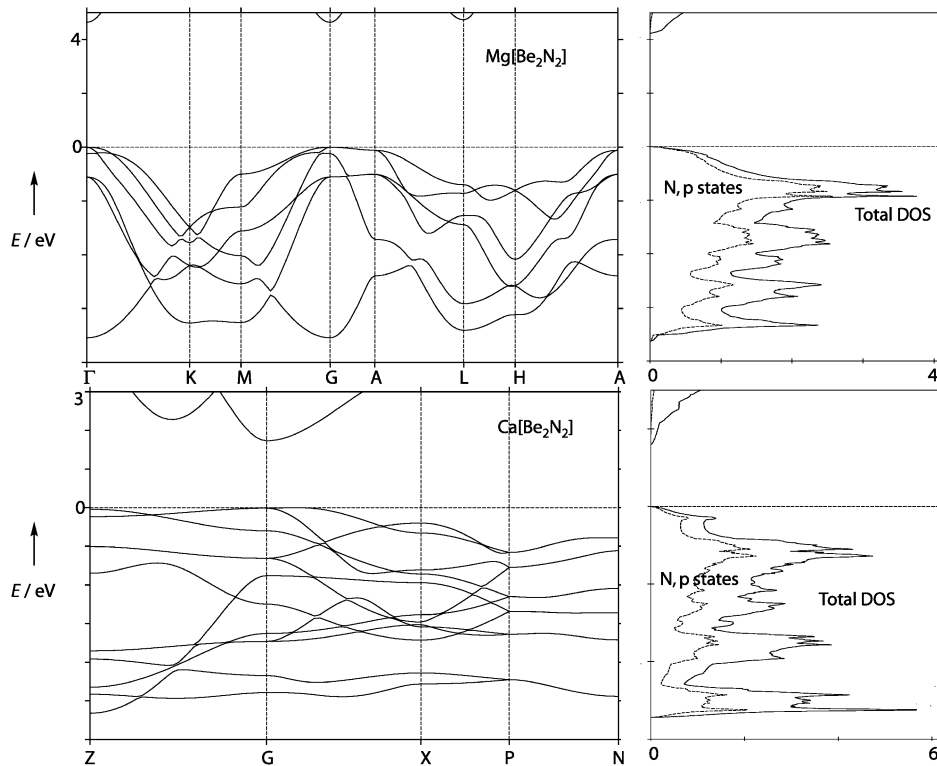


Figure 4. Electronic band structures along selected directions of the Brillouin zone (left) and DOS (right) of $\text{Mg}[\text{Be}_2\text{N}_2]$ (top) and $\text{Ca}[\text{Be}_2\text{N}_2]$ (bottom). See text for details.

Form a crystal-chemical point of view the nitridoberyllates can be assigned to a large class of compounds, which comprises complex anionic partial structures of lighter non-metallic elements, like borides and boride-carbides with eight valence electrons per pair of atoms ($[B_2^{2-}]$, $[BC^-]$). The nitridoberyllates extend this concept by the inclusion of a light metallic element (Be) in combination with nitrogen and by the formation of complex anionic partial structures of general formula $[BeN^-]$. A large number of such compounds with alkali or alkaline-earth metals contain planar anionic units like $Mg[B_2]$,^[28,29] $Mg[B_2C_2]$,^[30] or $Li[BC]^{[27]}$ with 6^3 nets; planar 4.8^2 nets are present for example in $Ca[B_2C_2]^{[12]}$ and in the nitridoberyllates of calcium and strontium presented in this work. Puckered 4.8^2 nets are present in the crystal structure of $Li[BeN]$.^[1] Having puckered nets connected into double layers and a peculiar nitrogen bonding situation, $Mg[Be_2N_2]$ occupies a special position in this class of compounds. It is expected that interesting physical properties will appear after appropriate chemical modifications.

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