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MgNB$_9$, a new magnesium nitridoboride

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The structure of a new magnesium nitridoboride, MgNB$_9$, has been refined from single-crystal X-ray data. The Mg and N atoms lie on sites with crystallographic $3m$ symmetry. The structure consists of two layers alternating along the c axis. The NB$_6$ layer, with B$_{12}$ icosahedra, has the C$_2$B$_{13}$ structure type. Within this layer, boron icosahedra are bonded to N atoms, each coordinating to three boron polyhedra. Another MgB$_3$ layer, with B$_6$ octahedra, does not belong to any known structure type. The boron icosahedra and octahedra are connected to each other, thus forming a three-dimensional boron framework.

Comment

The discovery of superconductivity at $T_c \simeq 39$ K in MgB$_2$ (Nagamatsu *et al.*, 2001) has attracted great interest from the scientific and applications viewpoints. Single crystals are indispensable for studies of the physical properties of this compound. During attempts to grow single crystals of MgB$_2$ in a BN crucible, black hexagonal prism-shaped crystals were obtained. Energy-dispersive X-ray analysis showed the presence of Mg, B and N. Single-crystal analysis was performed to determine the structure and composition of this new phase, MgNB$_9$, and the results are presented here.

The structure of MgNB$_9$ is shown in Fig. 1. It may be considered as an intergrowth of two layers, *viz*. NB$_6$ (Fig. 2) and MgB$_3$ (Fig. 3*a*). The Mg and N atoms lie on sites with crystallographic $3m$ symmetry. Boron polyhedra from different layers are connected to each other, thus forming a rigid three-dimensional framework with channels along the [110] direction, in which Mg and N atoms are located. Probably for this reason, the atomic displacement parameters of the B and N atoms are very small ($U_{ii} \sim 0.0035$ Å^2), especially compared with those of Mg (U_{11} = 0.013 Å^2 and U_{33} = 0.006 Å^2).

The NB$_6$ layer is similar to the CB$_6$ layer in the structure of C$_2$B$_{13}$ (Will & Kossobutzki, 1976). It is built of boron icosahedra which are interconnected within the layer through the N atoms, and each N atom is bonded to three boron polyhedra, with a B—N—B angle of 115.22 (3)°. Each B atom in this layer forms five bonds within the icosahedron, and one bond with either an N atom (B1) or a B atom from the boron octahedron of another layer (B2). All B—B distances are typical for this type of compound.

It is not useful to compare known B—N distances with those of MgNB$_9$. Usually, boron nitrides are obtained in nitrogen-rich regions and have quite different mutual coordination of the B and N atoms. For the most part, B—N bonds in boron nitrides are much shorter (1.34–1.45 Å) than in MgNB$_9$ (1.524 Å), but in some cases may be as long as 1.50 Å (UBN; Klesnar & Rogl, 1991) or 1.54 Å (PrBN$_2$; Rogl & Klesnar, 1992).

Two neighbouring N atoms are bonded to Mg atoms from different layers and are shifted from the average layer plane in different directions. Mg—N distances in nitrides and boron nitrides vary in the wide range 1.91–2.18 Å, but the most reliable data give the range 2.03–2.15 Å for both nitrides (Mg$_3$N$_2$; Partin *et al.*, 1997) and boron nitrides (Mg$_3$BN$_3$;

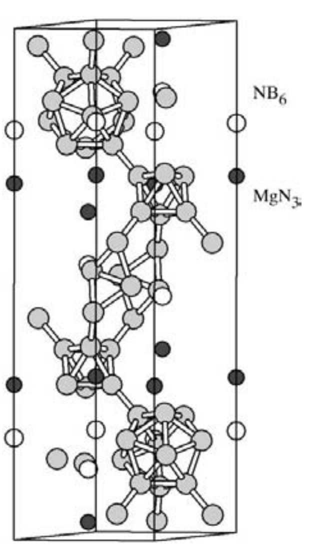

Figure 1
The structure of MgNB$_9$. White circles indicate N, grey circles indicate B and dark-grey circles indicate Mg atoms.

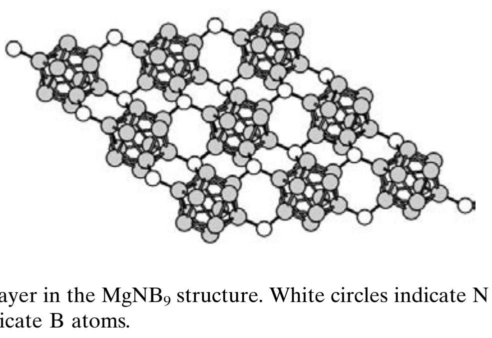

Figure 2
The NB$_6$ layer in the MgNB$_9$ structure. White circles indicate N and grey circles indicate B atoms.

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Hiraguchi *et al.*, 1991), which is about the same as was found in the present study (Table 1).

A structural type for the other layer is unknown to date, although structures with a boron octahedral framework do exist. The CaB_6 structural type (von Stackelberg & Neumann, 1932) may be taken as a starting point if we consider its octahedral layer perpendicular to the body diagonal of the cubic unit cell (Fig. 3*b*), but the orientations of the octahedra are different; in $MgNB_9$, they are rotated 30° around the $\overline{3}$ axis of the hypothetical cubic unit cell compared with the CaB_6 structure. Structural transformations are known for borides. In the structure of Li_2B_6 (von Schnering *et al.*, 1999), the boron octahedra are rotated around the fourfold axis, which results in a reduction of symmetry from cubic to tetragonal.

For $MgNB_9$, all the B atoms in the octahedra form four bonds within the polyhedron and one bond to an icosahedron of the other layer. All bonds are typical for such a polyhedron. The B2—B3 interpolyhedron distance tends to be somewhat shorter than the intrapolyhedron bonds, which is the same as is observed in structures with the octahedral network.

The Mg coordination polyhedron consists of two spheres. The inner sphere is a trigonal pyramid formed by three B atoms and the N atom. These Mg—B distances are about the same as in MgB_2, namely 2.50 Å (Jones & March, 1954). The directions of the Mg—N and Mg—B bonds correlate with the smallest displacements of the Mg atom, clearly seen in the probability density function maps (Fig. 4). The Mg—B distances in the outer sphere are much longer and probably weak. Similar coordination is typical for boron-rich compounds of Mg or Al (*e.g.* Higashi & Ito, 1983).

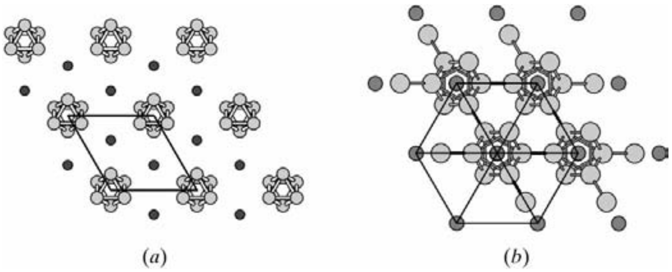

Figure 3
(*a*) The MgB_3 layer in the $MgNB_9$ structure and (*b*) the structure of CaB_6 viewed along [111]. White circles indicate N, grey circles indicate B and dark-grey circles indicate Mg or Ca atoms.

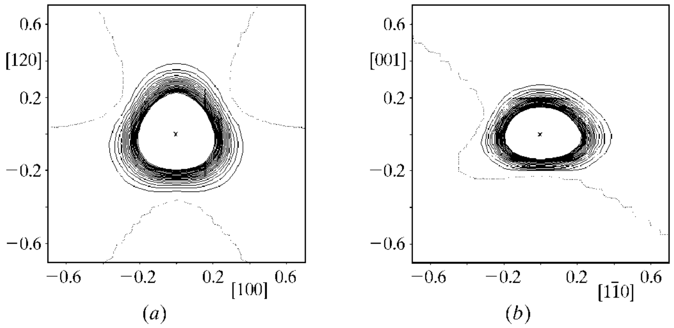

Figure 4
The probability density function map at the Mg site, showing (*a*) the *xy* section and (*b*) the *xz* section. Contours are drawn at 1% of the highest probability and the dotted line is the 0 level.

Experimental

Mg (99%) and amorphous B (99.99%) were used as the starting materials. A mixture of Mg and B in a molar ratio of 5:1 (total mass ~1 g) was placed in a BN crucible (inside diameter 6 mm, height 37.5 mm). The crucible was placed in a tungsten container and subjected to a high-pressure–high-temperature reaction in a high-gas-pressure apparatus (Karpinski *et al.*, 1999). First, argon pressure was applied, and then the temperature was raised to 1873 K at a rate of 600 K h^{-1}. The sample was maintained at this temperature for 1 h and then cooled from 1873 to 1773 K at a rate of 60 K h^{-1} under 100 MPa of argon. Below 1773 K, the sample was cooled to room temperature at a rate of 600 K h^{-1}. After crushing the crucible, the product was heated *in vacuo* at 1023 K for 15 min to remove Mg. Black single crystals of $MgNB_9$ were extracted mechanically (maximum size 0.3 × 0.3 × 0.2 mm). Energy-dispersive X-ray analysis was performed on a Jeol 840 microscope.

Crystal data

$MgNB_9$
$M_r = 135.60$
Trigonal, $R\overline{3}m$
$a = 5.4960$ (2) Å
$b = 5.4960$ (2) Å
$c = 20.0873$ (16) Å
$V = 525.47$ (5) $Å^3$
$Z = 6$
$D_x = 2.570$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 12.5$–25.7°
$\mu = 0.28$ mm^{-1}
$T = 293$ K
Prism, black
0.22 × 0.19 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/1.33\theta$ scans
Absorption correction: Gaussian (*JANA*2000; Petříček & Dušek, 2000)
$T_{min} = 0.950$, $T_{max} = 0.973$
3520 measured reflections
712 independent reflections

630 reflections with $I > 3\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 50°$
$h = 0 \rightarrow 11$
$k = -11 \rightarrow 10$
$l = -43 \rightarrow 43$
1 standard reflection
frequency: 120 min
intensity decay: none

Refinement

Refinement on F
$R = 0.017$
$wR = 0.035$
$S = 1.05$
630 reflections

28 parameters
$w = 1/[\sigma^2(F) + 0.0009F^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.33$ e $Å^{-3}$
$\Delta\rho_{min} = -0.23$ e $Å^{-3}$

Table 1
Selected interatomic distances (Å).

Mg—N	2.0818 (7)	B1—B2	1.8038 (5)
Mg—B1	2.8398 (6)	B1—B2^{iii}	1.8006 (7)
Mg—B2^{i}	2.7928 (6)	B2—B2^{iv}	1.7800 (4)
Mg—B3^{i}	2.5423 (5)	B2—B3	1.6974 (5)
Mg—B3^{ii}	2.8106 (4)	B3—B3^{v}	1.7489 (4)
N—B1	1.5240 (4)	B3—B3^{vi}	1.7733 (6)
B1—B1^{iii}	1.8055 (7)		

Symmetry codes: (i) $x - \frac{1}{3}, y - \frac{2}{3}, \frac{1}{3} + z$; (ii) $-\frac{1}{3} - x, \frac{1}{3} - y, \frac{1}{3} - z$; (iii) $y - \frac{1}{3}, \frac{1}{3} - x + y, \frac{1}{3} - z$; (iv) $1 - y, 1 + x - y, z$; (v) $-y, x - y, z$; (vi) $y, -x + y, -z$.

The structure was refined in an isotropic approximation down to $R = 0.044$ and then in an anisotropic approximation down to $R = 0.019$. A difference Fourier synthesis revealed the highest residual peaks in the vicinity of the Mg site alternating with negative regions. Anharmonic displacement parameters were refined up to the sixth order. Anharmonic atomic displacement parameters used in the program were based on the Gram–Charlier expansion of the structure factor [$Cijk = Cijk \times 10^3$, $C111 = -0.0027$ (3), $C112 = C111/2$, $C113 = -0.00024$ (5), $C122 = -C112$, $C123 = C113/2$, $C133 = 0$, $C222 = -C111$, $C223 = C113$, $C233 = 0$, $C333 = 0.000013$ (5) Å^3]. All parameters of the fourth order and higher did not exceed 3σ and resulted in rather high negative regions in the probability density function maps. For this reason, only the third-order anharmonic terms were refined. The probability density function map for the Mg atom is presented in Fig. 4. Such refinement reduced the R factor from 0.019 to 0.017 and the residual peaks were halved. An isotropic extinction parameter was refined. Its value was small and $\sim\sigma$, and it was not included in the final refinement.

Data collection: *CAD*-4 *Manual* (Enraf–Nonius, 1988); cell refinement: *CAD*-4 *Manual*; data reduction: *JANA*2000 (Petříček & Dušek, 2000); program(s) used to solve structure: *CSD* (Akselrud *et al.*, 1989); program(s) used to refine structure: *JANA*2000; molecular graphics: *ATOMS for Windows* (Dowty, 1998); software used to prepare material for publication: *JANA*2000.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1376). Services for accessing these data are described at the back of the journal.

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