

non-centrosymmetric properties of these compounds. Alone it cannot account for the e.s.d.'s obtained for x . Clearly the polarity, or more precisely the non-enantiomorphic component of the non-centrosymmetric part of the electron density, is the predominant component which has been determined by x .

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Structure of Gd₃Ru₄Al₁₂, a New Member of the EuMg_{5.2} Structure Family with Minority-Atom Clusters

BY R. E. GLADYSHEVSKII, O. R. STRUSIEVICZ,* K. CENZUAL AND E. PARTHÉ

Laboratoire de Cristallographie, Université de Genève, 24 quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland

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Abstract

Gd₃Ru_{4+x}Al_{12-x} [$x = 0.13$ (2)], $M_r = 1209.44$, hexagonal, $hP38$, $P6_3/mmc - kh^2g fba$ (No. 194), $a = 8.8142$ (6), $c = 9.5692$ (9) Å, $V = 643.8$ (1) Å³, $Z = 2$, $D_x = 6.239$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 20.330$ mm⁻¹, $F(000) = 1056$ (1), $T = 293$ K, $wR = 0.023$ for 338 contributing unique reflections. Gd₃Ru₄Al₁₂ is a substitution variant of the Sc₃Ni₁₁Ge₄ structure which is a partly disordered variant of the Sc₃Ni₁₁Si₄ type, all three structures being ternary substitution derivatives of the EuMg_{5.2} or ErZn₅ types. Contrary to the related structure types, in Gd₃Ru₄Al₁₂ both Wyckoff sites 2(*a*) and 2(*b*) have full occupation, *i.e.* an ordered arrangement of alternate Ru and Al atoms is observed along the c axis. The structure of Gd₃Ru₄Al₁₂ is built up of two kinds of layers perpendicular to [001]: planar layers of composition Gd₃Al₄ and puckered layers of composition Ru₄Al₈. Similar layers are found in

cubic Hf₆Ni₇Al₁₆, a ternary substitution variant of Th₆Mn₂₃, as well as in hexagonal Sr₉Mg₃₈ and BaLi₄.

Introduction

The Gd–Ru–Al system has not been studied and no ternary compounds have been reported so far. Of the related systems with different transition metals from the Fe, Co or Ni groups, the largest number of phases have been identified in the Gd–Ni–Al system (Rykhali', Zarechnyuk & Marych, 1978; Gladyshevskii & Parthé, 1992; Gladyshevskii, Cenzual, Flack & Parthé, 1993). Of the eleven reported compounds, five form in the narrow concentration region from 7.7 to 16.7 at.% Gd and from 58.3 to 70.4 at.% Al. We identified a phase in the corresponding region of the Gd–Ru–Al system and determined its crystal structure.

Experimental

Crystals were found in a sample of nominal composition GdRu₂Al₃, prepared from high-purity elements

* Permanent address: Department of Mineralogy, Babes-Bolyai University, 1 Kogalniceanu Street, RO-3400 Cluj-Napoca, Romania.

($\geq 99.9\%$) by arc melting under an argon atmosphere (weight loss 0.2%) and annealed at 1073 K for two weeks in a silica tube under an argon atmosphere (400 mm Hg). A needle-like single crystal [dimensions $\pm(100)$: 0.030, $\pm(010)$: 0.030, $\pm(001)$: 0.092 mm] was mounted on a Philips PW1100 automatic four-circle diffractometer, Mo $K\alpha$ radiation with graphite monochromator. The unit-cell parameters were refined from 2θ values of 21 reflections (Mo $K\alpha$, $\lambda = 0.71073 \text{ \AA}$, $18 < 2\theta < 35^\circ$). 1564 reflections were collected out to $(\sin\theta/\lambda) = 0.702 \text{ \AA}^{-1}$ ($0 \leq h \leq 10$, $0 \leq k \leq 10$, $0 \leq l \leq 13$ and the anti-reflections) in the ω - 2θ scan mode, yielding 392 unique reflections ($R_{\text{int}} = 0.054$). Two standard reflections, $00\bar{4}$ and 004 , were measured showing maximum intensity variations of 1.1%. An absorption correction was made using *LSABS* (Blanc, Schwarzenbach & Flack, 1991) with maximum and minimum transmission factors of 0.5638 and 0.4615. The anomalous-dispersion coefficients were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Systematic absences led to the following possible space groups: $P6_3mc$, $P6_2c$ and $P6_3/mmc$ (*International Tables for Crystallography*, 1983, Vol. A). The structure was solved in space group $P6_3/mmc$ by *MULTAN87* (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987) and confirmed by least-squares refinements based on $|F|$ values. A partial substitution by Ru was found for one Al site. 26 variables, including anisotropic displacement parameters, refined to $R = 0.031$ and $wR = 0.023$ [$w = 1/\sigma^2(|F_{\text{rel}}|)$, $S = 1.511$], considering 338 contributing unique reflections with $|F_{\text{rel}}| > 3\sigma(|F_{\text{rel}}|)$. A secondary extinction correction parameter (Gaussian distribution of mosaic spread) refined to $G = 0.011$ (1). The maximum shift/e.s.d. in the last cycle was 0.5×10^{-4} ; final residual electron density $+4.3$ (-2.9) $e \text{ \AA}^{-3}$. The programs used for the data reduction and structure refinements are all from the *XTAL3.0* system (Hall & Stewart, 1990). The final atomic positional parameters, standardized by *STRUCTURE TIDY* (Gelato & Parthé, 1987) and the (equivalent) isotropic displacement parameters are listed in Table 1.* The interatomic distances up to 4 Å are given in Table 2.

Discussion

The hexagonal structure of $\text{Gd}_3\text{Ru}_4\text{Al}_{12}$ is a substitution variant of isopointal $\text{Sc}_3\text{Ni}_{11}\text{Ge}_4$ (Andrusyak, 1988), which itself is a disordered variant of the

* Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55865 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU0343]

Table 1. *Atomic positional and displacement parameters for $\text{Gd}_3\text{Ru}_4+x\text{Al}_{12-x}$ [$x = 0.13$ (2)] with space group $P6_3/mmc$*

The equivalent isotropic displacement parameters are expressed as $U_{\text{eq}} = (1/3)\sum_i \Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$. E.s.d.'s are given in parentheses.

Site		x	y	z	U_{eq} ($\text{Å}^2 \times 10^2$)
Al(1)	12(k)	0.1622 (2)	2x	0.5762 (3)	0.93 (9)
	6(h)	0.19285 (5)	2x	1/4	0.78 (2)
Al(2)†	6(h)	0.5637 (3)	2x	1/4	0.8 (1)
	6(g)	1/2	0	0	0.68 (3)
Al(3)	4(f)	1/3	2/3	0.0116 (5)	0.8 (1)
Al(4)	2(b)	0	0	1/4	0.7 (2)
Ru(2)	2(a)	0	0	0	0.64 (5)

† Site occupancy $\text{Al}_{0.956(7)}\text{Ru}_{0.044(7)}$, atomic displacement parameter refined isotropically.

Table 2. *Interatomic distances up to 4 Å in $\text{Gd}_3\text{Ru}_4\text{Al}_{12}$ with e.s.d.'s in parentheses*

Gd—	Al(4)	2.944 (1)	Al(3)—	3Ru(1)	2.547 (1)
	2Al(2)	3.070 (2)		3Al(1)	2.744 (3)
	2Al(3)	3.132 (4)		3Al(2)	2.956 (5)
	2Al(1)	3.156 (3)		3Gd	3.132 (4)
	4Al(1)	3.206 (2)			
	4Ru(1)	3.368 (1)	Al(4)—	2Ru(2)	2.392 (1)
	2Gd	3.715 (1)		3Gd	2.944 (1)
	2Ru(2)	3.794 (1)		6Al(1)	2.983 (3)
				6Al(1)	3.984 (3)
Al(1)—	Ru(2)	2.582 (3)			
	2Ru(1)	2.680 (2)			
	Al(3)	2.744 (3)	Ru(1)—	2Al(3)	2.547 (1)
	2Al(2)	2.821 (4)		2Al(2)	2.582 (2)
	2Al(1)	2.874 (2)		4Al(1)	2.680 (2)
	Al(4)	2.983 (3)		4Gd	3.368 (1)
	Gd	3.156 (3)			
	2Gd	3.206 (2)			
	Al(1)	3.326 (4)	Ru(2)—	2Al(4)	2.392 (1)
	Al(4)	3.984 (3)		6Al(1)	2.582 (3)
			6Gd	3.794 (1)	
Al(2)—	2Ru(1)	2.582 (2)			
	2Al(2)	2.724 (4)			
	4Al(1)	2.821 (4)			
	2Al(3)	2.956 (5)			
	2Gd	3.070 (2)			

$\text{Sc}_3\text{Ni}_{11}\text{Si}_4$ type (Kotur, Sikiritsa, Bodak & Gladyshevskii, 1983). All three structures are ternary derivatives of ordered ErZn_5 (Fornasini, 1971) and partly disordered $\text{EuMg}_{5.2}$ (Erassme & Lueken, 1987). The site occupations in these five closely related structure types are compared in Table 3. It can be seen that in $\text{Sc}_3\text{Ni}_{11}\text{Ge}_4$ Wyckoff sites 2(a) and 2(b) are partially occupied, the sum of their occupations being equal to 100%. In $\text{Sc}_3\text{Ni}_{11}\text{Si}_4$ no atoms were detected in Wyckoff position 2(a) whereas full occupation was assumed for 2(b). However a slight residual electron-density peak in 2(a) was reported and a partial disorder may occur for this compound as well. Problems in determining the atom arrangement along the c axis were mentioned also for the binary parent types. Thus, in the first structure proposal for 'EuMg₅' (Mühlpfordt, 1970), only one site on the c axis was found, *i.e.* Wyckoff position 2(a). However, in a more recent refinement three partially occupied sites, 2(a), 2(b) and 4(e) with $z = 0.0883$, were detected, leading to the composition $\text{EuMg}_{5.2}$. For ErZn_5 , reported as isotypic to 'EuMg₅', weak

Table 3. Atom-site occupation in Gd₃Ru_{4+x}Al_{12-x}, Sc₃Ni₁₁Ge₄, Sc₃Ni₁₁Si₄, EuMg_{5.2} and ErZn₅ with space group P6₃/mmc

Site	Gd ₃ Ru _{4+x} Al _{12-x}	Sc ₃ Ni ₁₁ Ge ₄	Sc ₃ Ni ₁₁ Si ₄	EuMg _{5.2}	ErZn ₅
12(k)	Al	Ni	Ni	Mg	Zn
6(h)	Gd	Sc	Sc	Eu	Er
6(h)	Al _{0.956} Ru _{0.044}	Ni	Ni	Mg	Zn
6(g)	Ru	Ge	Si	Mg	Zn
4(f)	Al	Ni	Ni	Mg	Zn
4(e)				Mg _{0.26}	
2(b)	Al	Ge _{0.72}	Si	Mg _{0.77}	
2(a)	Ru	Ge _{0.28}		Mg _{0.40}	Zn

reflections were observed, which indicated the existence of a possibly ordered superstructure with a six-fold *c* parameter. In the structure of the new compound Gd₃Ru₄Al₁₂ both Wyckoff sites 2(*a*) and 2(*b*) have full occupation. The *c* parameter of this structure is relatively large in comparison to the structures discussed above and corresponds to an Ru—Al distance of 2.39 Å. Ru—Al distances of similar magnitude were observed in Ru₄Al₁₃ with the Fe₄Al₁₃ structure type (Edshammar, 1965).

Whilst not a layer structure in the conventional sense, Gd₃Ru₄Al₁₂ can be considered as built up of two kinds of layer perpendicular to [001], shown in Fig. 1. In the first kind of layer the Gd atoms form distorted Kagome nets with larger and smaller triangles, the edge length of the smaller ones corresponding to a Gd—Gd contact distance (3.72 Å). The Al(2) atoms are arranged in equilateral triangles inside the hexagons of the Kagome nets, with an Al—Al distance of 2.72 Å. As can be seen from Table 1, a slight substitution by Ru (which will be ignored in the following) was found for this site. The large Gd-atom triangles are centred by the atoms in the Al(4) site. Such planar layers of composition Gd₃Al₄ are located at $z = \frac{1}{4}$ and $z = \frac{3}{4}$, consecutive layers being related by the 6₃ axis. In the second kind of layer the Ru atoms form a triangular mesh. All triangles of the mesh are centred by Al atoms, located either approximately in the plane [site Al(3)], or above or below it [site Al(1)]. These puckered layers, with their central plane at $z = 0$ and $z = \frac{1}{2}$, have the composition Ru₄Al₈, leading to the overall composition 2Gd₃Ru₄Al₁₂ = 2Gd₃Al₄ + 2Ru₄Al₈.

The triangular clusters formed by the rare-earth-metal atoms in the structures of ErZn₅, EuMg_{5.2} and their ternary derivatives have been pointed out by several authors (e.g. Erassme & Lueken, 1987), contact distances between minority atoms being quite unusual. Triangles built up from minority atoms with large atomic radii are also observed in BaLi₄ (Wang, Kanda, Miskell & King, 1965). The structure of Sr₉Mg₃₈ (Merlo & Fornasini, 1982) contains isolated Sr-atom triangles and octahedra, the latter being formed by two superposed Sr-atom triangles rotated by 60° with respect to each other. Minority-atom octahedra are also a characteristic feature of

the Th₆Mn₂₃ type (Florio, Rundle & Snow, 1952) and its ternary substitution derivatives Mg₆Cu₁₆Si₇ (Bergman & Waugh, 1956) and Hf₆Ni₇Al₁₆ (Ganglberger, Nowotny & Benesovsky, 1966). It is shown in Fig. 2 that all these structures contain layers similar to those described above for Gd₃Ru₄Al₁₂. The corresponding stacking sequences, using the notation introduced for close-packed layers, are indicated near the translation units of the layers. Upper-case letters stand for the Gd-, Hf-, Sr- and Ba-containing layers and lower-case letters for the puckered layers. Layers in stacking positions marked with primes are rotated by 60° around the centre of a small Gd-, Hf-, Sr- or Ba-atom triangle, with respect to layers in corresponding positions without primes.

It can be seen from Fig. 2 that the sequence *B'AC* is found in both Gd₃Ru₄Al₁₂ and Hf₆Ni₇Al₁₆. In the latter structure the sequence *B'AC* is transformed into *C'BA* and *A'cB* according to the rhombohedral translation. These packets are separated by a third kind of layer (indicated by Greek letters), built up of Ni atoms arranged in a regular Kagome net.

The stacking sequence *A'cBcA'* observed in Sr₉Mg₃₈ can be obtained by translation from the sequence *B'aCaB'* found in Gd₃Ru₄Al₁₂. As in Hf₆Ni₇Al₁₆, the packets are separated by a single Kagome-net layer. For Sr₉Mg₃₈ there is a doubt about the correct composition. In the early structure determination of 'SrMg₄' (Wang *et al.*, 1965), one atom site 4(*f*) was overlooked, leaving apparent vacancies in the puckered Mg-atom layers. In a recent refinement of a possibly isotypic pseudo-binary (Sr,Eu)—Mg compound, one more site [2(*d*)] was detected, leading to the refined composition (Sr_{0.67}Eu_{0.33})₃Mg₁₃ (Erassme & Lueken, 1987). The Mg atoms in this additional site, marked with stripes in Fig. 2, centre the remaining large-atom (Sr,Eu)

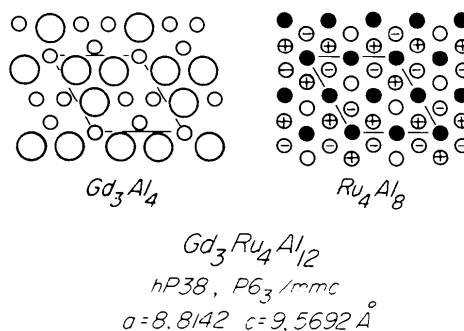


Fig. 1. The two kinds of layer perpendicular to [001] in Gd₃Ru₄Al₁₂. In the planar Gd₃Al₄ layer at $z = \frac{1}{4}$ large circles correspond to Gd and small circles to Al atoms. In the puckered Ru₄Al₈ layer at $z = 0$ black circles correspond to Ru atoms at $z = 0$, open circles to Al atoms at $z = \pm 0.012$ and circles marked with a plus or minus sign to Al atoms at $z = \pm 0.076$.

triangles. This site is directly comparable with the site in Wyckoff position 2(*b*) in $Gd_3Ru_4Al_{12}$ and other structures of the $EuMg_{5.2}$ structure family.

In $BaLi_4$ both kinds of layer, similar to those found in $Gd_3Ru_4Al_{12}$, contain vacancies. Those Li atoms of the puckered layers which are situated above or below a vacancy of a mixed layer are displaced towards this vacant site (directly comparable sites in the other structures being located approximately in the central plane of the layer).

As can be seen from Fig. 1, the centres of the Al-atom triangles and the Gd atoms in $Gd_3Ru_4Al_{12}$ form a distorted triangular mesh. Another kind of mixed layer where the centres of the Al-atom triangles form a regular triangular mesh together with

the rare-earth-metal atoms, was observed recently in the structures of two new aluminides, *i.e.* $ErNi_3Al_9$ (Gladyshevskii *et al.*, 1993) and $Y_2Co_3Al_9$ with a $Y_2Co_3Ga_9$ -type structure (Gladyshevskii, Cenzual & Parthé, 1992). These layers have the composition R_2Al_3 , the ratio of Al-atom triangles to rare-earth-metal atoms being 1:2, compared to 1:3 for the structures discussed here. Distorted Al_8 cubes are observed around the transition-metal atoms in all three aluminides.

Ignoring the two sites on the *c* axis, which were both found to contain Ge atoms in $Sc_3Ni_{11}Ge_4$, Table 3 shows that the Ru and Al atoms in $Gd_3Ru_4Al_{12}$ occupy those sites which in $Sc_3Ni_{11}Ge_4$ are occupied by Ge and Ni atoms, respectively. Such

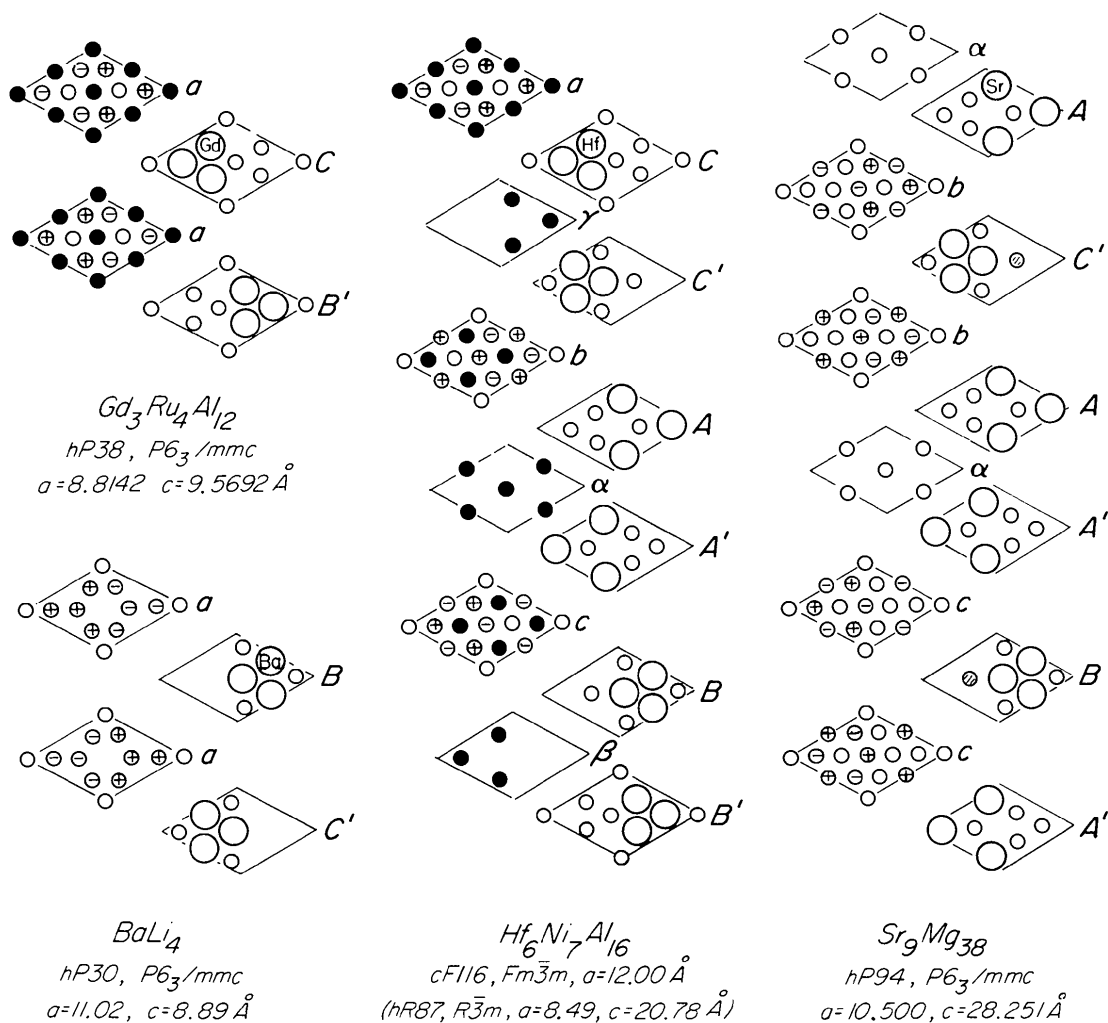


Fig. 2. The stacking of layers along [001] in $Gd_3Ru_4Al_{12}$, $Hf_6Ni_7Al_{16}$ (triple hexagonal cell), Sr_9Mg_{38} and $BaLi_4$. Large circles represent Gd, Hf, Sr or Ba atoms, and black circles Ru or Ni atoms. Atoms indicated with a plus or minus sign are situated above or below the central plane of the layer. Circles marked with stripes in the layers of Sr_9Mg_{38} indicate the additional site detected for $(Sr_{0.67}Eu_{0.33})_3Mg_{13}$. The letter near the translation unit of the layer stands for its relative stacking position. Layers with central plane at $z=0$ are shown on top.

a site exchange between transition-metal and main-group elements has been observed for several structure types (see *e.g.* Parthé & Chabot, 1984). As mentioned above, a site exchange is also observed for ternary silicide and aluminide substitution derivatives of Th₆Mn₂₃, the transition-metal element (Ni) in Hf₆Ni₇Al₁₆ occupying the same sites as the main-group element (Si) in Mg₆Cu₁₆Si₇. Ternary Ru-based aluminides of approximate composition R₆Ru₇Al₁₆ (R = Sc, Ti or Zr), have also been reported with this structure type (Markiv & Storozhenko, 1973).

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Structure of a High-Pressure Polymorph of Mg₃BN₃ Determined from X-ray Powder Data

BY HIDEO HIRAGUCHI,* HIROO HASHIZUME† AND SATOSHI SASAKI

Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Nagatsuta, Midori, Yokohama 227, Japan

AND SATOSHI NAKANO AND OSAMU FUKUNAGA

Department of Inorganic Materials, Faculty of Engineering, Tokyo Institute of Technology, Ookayama, Meguro, Tokyo 152, Japan

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Abstract

The crystal structure of magnesium boron nitride in a high-pressure phase, Mg₃NB₃(H), has been determined from X-ray powder diffraction data. The strategy used was: powder pattern indexing, extraction of integrated intensity data by peak decomposi-

tion, Patterson function calculation, trial-and-error model building and Rietveld refinement. The cell is orthorhombic (space group *Pmmm*, *Z* = 1) with *a* = 3.0933 (2), *b* = 3.1336 (2) and *c* = 7.7005 (5) Å. The structure contains linear NBN groups with an observed B—N interatomic distance of 1.34 Å which is 2% shorter than in the low-pressure form of the material, Mg₃NB₃(L). The double-bonded N=B=N molecular anions are believed to play an important role in the recently reported decomposition of

* Present address: The Tokyo Electric Power Co. Inc., 1–1–3 Uchisaiwaicho, Chiyoda, Tokyo 100, Japan.

† To whom all correspondence should be addressed.