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$Tb_2Ni_2Mg_3$: a new structure type derived from the $Ru_3Al_2B_2$ type

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Single crystals of diterbium dinickel trimagnesium, $Tb_2Ni_2Mg_3$, were synthesized from the elements by induction melting. The novel compound crystallizes in the space group *Cmmm* with one Mg atom of site symmetry *mmm* and the Tb, Ni and other Mg atom in *m*2*m* positions. This ternary compound represents a new structure type that is derived from $Ru_3Al_2B_2$ by way of Wyckoff site distribution. The two-layer structure of $Tb_2Ni_2Mg_3$ is a new representative of a homologous linear structure series of general formula $R'_{k+n}X_{2n}R''_{2m+k}$ based on structural fragments of the α-Fe, CsCl and AlB_2 structure types. The Tb atoms in the structure are enclosed in 17-vertex polyhedra, while rhombododecahedra and distorted rhombododecahedra surround the Mg atoms, and equatorially tricapped trigonal prisms form around the Ni atoms. All interatomic distances indicate metallic type bonding.

Comment

Recently, rare-earth transition metal intermetallics have been studied because of their particular mechanical and physical properties as superconductors, batteries, magnets, magnetocaloric materials, *etc*. They also have great potential as hydrogen storage materials. Mg-modified alloys look to be particularly effective because of higher hydrogen capacity with lower density and cost. A number of recent studies of such materials have been reported. Kadir *et al.* (1997) have studied a series of hydrogen storage alloys of stoichiometry $(RE)Ni_9Mg_2$ (RE = La–Nd, Sm and Gd) that crystallize in the $PuNi_3$ structure. The hydrogen capacity of $(RE)Ni_4Mg$ (RE = Y, La and Nd) compounds with the $MgCu_4Sn$ structure type vary from 3.4 to 4.02 H atoms per formula unit under different conditions (Aono *et al.*, 2000; Guénée *et al.*, 2003). It was shown that the $LaNi_2Mg$ ternary compound with the Heusler-type structure adsorbs hydrogen, forming the quaternary metal hydride $LaMg_2NiH_7$ (Renaudin *et al.*, 2003). Li *et al.* (2004) reported that the $La_{1.5}Mg_{17}Ni_{0.5}$ alloy adsorbs 5.4 wt. % H at 573 K at excellent speed without any activation process. The electrochemical performances of a number of La–Ni–Mg alloys with high Ni content show promising electrode properties with higher discharge capacity (~400–410 mAh g^{-1}) than those employing alloys commonly adopted at present (Kohno *et al.*, 2000; Liao *et al.*, 2003).

The crystal structure, chemical bonding and physical properties of the series of $RE_2\{Cu,Ni,Pd\}_2Mg$ ternaries with Mo_2FeB_2 structure type were investigated by Lukachuk & Pöttgen (2003). The new non-metallic $La_2MgNi_2H_8$ (1.89 wt. % H) complex hydride was obtained readily by hydrogenation of La_2MgNi_2 (Chotard *et al.*, 2006). Detailed investigation of the constitutional properties of La–Ni–Mg at 673 K (De Negri *et al.*, 2005) and La–Cu–Mg (De Negri *et al.*, 2007) have indicated a great number of novel ternary phases that potentially could be hydrogen storage materials. Under such conditions, the accurate determination of the crystal structure of new intermetallics is the basic requirement for a better understanding of their physical properties. In this paper, the results of our recent structure investigation of the $Tb_2Ni_2Mg_3$ ternary compound, obtained during a systematic investigation of the Tb–Ni–Mg system at 673 K, are reported.

The $Ru_3Al_2B_2$ structure type was discovered by Jung & Schweitzer (1986). Since then, other representatives of this structure type among intermetallics have not been found. The title compound represents a new structure type that results from a site redistribution of the $Ru_3Al_2B_2$ structure, where the Al (4*j*) site is now occupied by Mg atoms. Two Ru-atom positions (2*a* and 4*i* sites) are redistributed among Mg and Tb atoms, respectively. The B (4*j*) site corresponds to the Ni-atom positions. Thus, the compound could be represented also as $(Tb_2Mg)Mg_2Ni_2$. The unit-cell projection of $Tb_2Ni_2Mg_3$ on to the (001) plane with delineated coordination polyhedra is

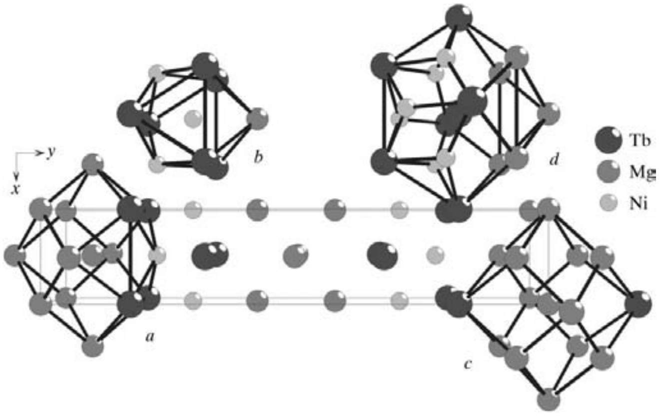

Figure 1
A perspective view of the unit-cell projection of $Tb_2Ni_2Mg_3$ on to the (001) plane. Coordination polyhedra of Tb (*d*), Mg1–Mg2 (*a* and *c*) and Ni (*b*) are shown.

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shown in Fig. 1. The first coordination spheres [including bonding interactions up to 4 Å according to the empirical rule of $2^{1/2} \times \delta_{\rm min}$ of Krypyakevich (1977)] of the atoms are normal for intermetallics. The Tb atoms (site symmetry *m*2*m*) are surrounded in the structure by 17 adjacent atoms, *i.e.* [(Tb1)$Ni_6Mg_5Tb_6$] (*d*). A rhombododecahedron [(Mg2)-Tb_2Mg_{12}] (*c*) and distorted rhombododecahedron [(Mg1)-Tb_4Mg_9Ni] (*a*) surround atoms Mg2 (*mmm*) and Mg1 (*m*2*m*), respectively. The Ni atoms (*m*2*m*, bonding interaction < 3.6 Å) are characterized by equatorially tricapped trigonal prisms

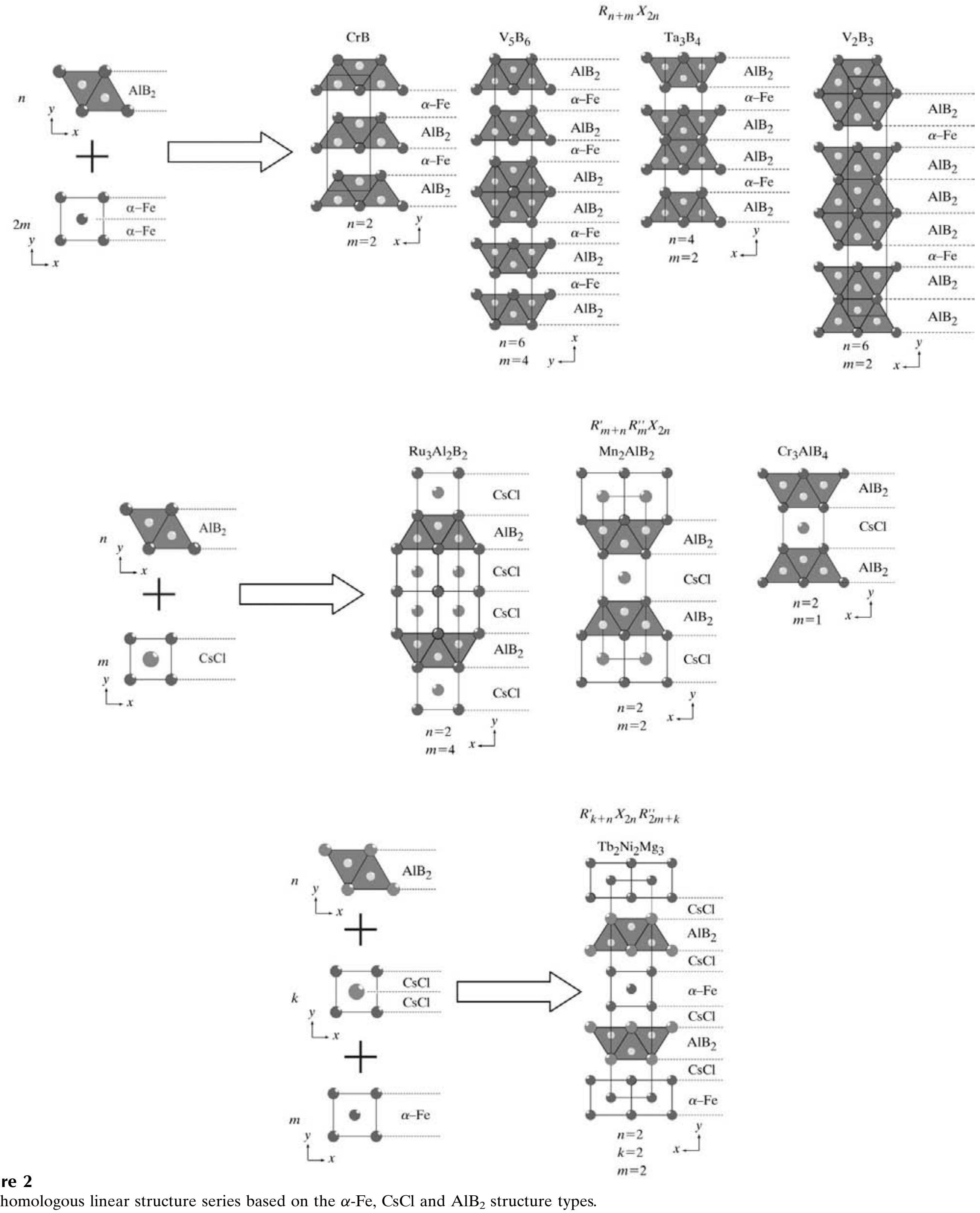

Figure 2
The homologous linear structure series based on the α-Fe, CsCl and AlB_2 structure types.

[(Ni1)Tb_6Ni_2Mg] (*b*). The structure of $Tb_2Ni_2Mg_3$ belongs to class No. 10 [coordination number 6 + *n* (*n* = 0–5) for the smallest atom, trigonal prism and its derivatives as coordination polyhedra] according to the classification scheme of Krypyakevich (1977). The interatomic distances (Table 1) are in good correlation with the sums of the atomic radii (Emsley, 1991) and indicate metallic type bonding (the shortest Tb—Ni distance is 2.812 Å, which is 93.4% of the sum of the atomic radii).

According to Krypyakevich (1977), structure types belong to homologous series if they are composed of the same multiple fragments and differ between themselves by quantitative ratios of these fragments, so that a general formula and ratio describes all structures of the homologous series. The linear structure series is assigned when the two-dimensional segments (infinite slabs) of constituent fragments are stacked one-dimensionally along a stacking direction. Kuz'ma (1983) has described a homologous linear structure series of borides of general formula $R'_{n+m}X_{2n}$, with constituent fragments of the α-Fe and AlB_2 structure types (*n* is the number of blocks of AlB_2-type trigonal prisms and *m* is the number of half unit-cell blocks of α-Fe structure type). This series (Fig. 2) includes the CrB (*n* = 2 and *m* = 2), V_5B_6 (*n* = 6 and *m* = 4), Ta_3B_4 (*n* = 4 and *m* = 2) and V_2B_3 (*n* = 6 and *m* = 2) structure types. Another homologous linear structure series consists of fragments of the CsCl and AlB_2 structure types (Fig. 2) with formula $R'_{n+m}R''_{m}X_{2n}$ (*n* is the number of blocks of AlB_2-type trigonal prisms and *m* is the number of blocks of CsCl-type cubes), including $Ru_3Al_2B_2$ (*n* = 2 and *m* = 4), Mn_2AlB_2 (*n* = 2 and *m* = 2) and Cr_3AlB_4 (*n* = 2 and *m* = 1). $Tb_2Ni_2Mg_3$ can be viewed as the first representative of a novel linear structure series based on the α-Fe, CsCl and AlB_2 structure types combined. The general formula of this series is $R'_{k+n}X_{2n}R''_{2m+k}$ (*n* is the number of blocks of AlB_2-type trigonal prisms, *m* is the number of unit-cell blocks of α-Fe structure type and *k* is the number of blocks of CsCl-type cubes). For $Tb_2Ni_2Mg_3$ itself, *m* = *n* = *k* = 2. $Tb_2Ni_2Mg_3$ belongs to the family of two-layer compounds, along with more than 70 other inorganic structure types (mainly borides) according to *TYPIX* (Parthé *et al.*, 1993–1994).

Experimental

The alloys were prepared by induction melting of stoichiometric amounts of the constituent metals (purity > 99.9% for Tb and Mg, and 99.98% for Ni) placed together into outgassed tantalum crucibles sealed by arc-welding under conditions of pure argon. The alloys were then annealed in an evacuated quartz tube at 673 K for three weeks. After annealing, the samples could be readily separated from the tantalum crucible. No side reaction of the samples with the crucible was detected. The samples, in the form of compact buttons as well as fine-grained powders, were stable against air and moisture influence. The sample preparation method is completely reproducible. A series of alloys containing the $Tb_2Ni_2Mg_3$ phase were analyzed by scanning electron microscopy and energy-dispersive X-ray spectroscopy (EDXS) in order to study their microstructure and phase composition (with ±0.5 at.% accuracy). A single crystal was extracted from an alloy of nominal composition $Tb_{27}Ni_{22}Mg_{51}$ (consisting mainly of the $Tb_2Ni_2Mg_3$ phase). An average result of the EDXS analysis for the bulk samples is 29.6 at.% Tb, 29.0 at.% Ni and 41.4 at.% Mg, which compares well with the composition obtained from the structural refinement.

Crystal data

$Tb_2Ni_2Mg_3$
M_r = 508.19
Orthorhombic, *Cmmm*
a = 3.9788 (7) Å
b = 21.203 (4) Å
c = 3.6583 (7) Å
V = 308.62 (10) Å^3
Z = 2

D_x = 5.469 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 28.80 mm^{-1}
T = 295 (2) K
Irregularly shaped, metallic dark grey
0.1 × 0.08 × 0.04 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
ω scans
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2005)
T_{min} = 0.075, T_{max} = 0.313

940 measured reflections
213 independent reflections
199 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 26.4°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.078
S = 1.10
213 reflections
16 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0609P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 2.23 e Å^{-3}
$\Delta\rho_{min}$ = −1.21 e Å^{-3}

Table 1
Selected bond lengths (Å).

Tb1—Ni1^{i}	2.8118 (7)	Tb1—Tb1^{iv}	3.9788 (7)
Tb1—Ni1	2.9735 (17)	Ni1—Ni1^{i}	2.533 (3)
Tb1—Mg1^{i}	3.386 (4)	Ni1—Mg1	2.817 (6)
Tb1—Tb1^{ii}	3.6583 (7)	Mg1—Mg2^{v}	3.193 (3)
Tb1—Tb1^{iii}	3.7007 (13)	Mg1—Mg1^{vi}	3.400 (12)
Tb1—Mg2	3.7405 (9)		

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

Systematic absences indicated the possible space groups *C*222 (No. 21), *Cmm*2 (No. 35), *Amm*2 (No. 38) and centrosymmetric *Cmmm* (No. 65). A statistical test of the distribution of the *E* values (Farrugia, 1999) suggested that the structure is non-centrosymmetric; however, following the advice of Marsh (1995), the structure solution and refinement were also performed in the centrosymmetric group. The results clearly indicated that $Tb_2Ni_2Mg_3$ crystallizes in the centrosymmetric space group *Cmmm*, since the solution and refinement in the non-centrosymmetric variants were not satisfactory. The occupancy parameters were refined for this structure in order to check for deviations from the ideal composition. No significant deviations were found. Hence, in the final refinement cycles of this structure, the ideal occupancy parameters were retained. Data were then refined with anisotropic displacement parameters for all atoms. The atomic coordinates were standardized using the *STRUCTURE TIDY* program (Gelato & Parthé, 1987). The final difference Fourier syntheses revealed no significant residual peaks; the highest maximum residual electron density is 2.23 Å from Tb and the deepest hole is 1.21 Å from Ni.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*

(Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3057). Services for accessing these data are described at the back of the journal.

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