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Key indicators

Single-crystal X-ray study
T = 295 K
Mean $\sigma(\text{Ge}-\text{Ge}) = 0.003 \text{ \AA}$
R factor = 0.042
wR factor = 0.082
Data-to-parameter ratio = 20.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Single crystals of didysprosium aluminium digermanide were synthesized from the corresponding elements by arc-melting in the presence of Ni. The new intermetallic compound crystallizes in the space group *P4/mbm* and adopts the Mo₂FeB₂ structure type, with all three crystallographically unique atoms in special positions of site symmetries *m.2m* (Dy and Ge) and *4/m..* (Al). The coordination polyhedra around the metal atoms are distorted pentagonal (Dy), tetragonal (Al) and trigonal (Ge) prisms with 7, 4 and 3 additional capping atoms, respectively.

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Comment

Ternary intermetallics of rare-earth metals with formulae *RE₂T₂X* and *RE₂X'₂X* (where *RE* is a rare earth metal, *T* is a transition metal, and *X* and *X'* are *p*-block elements) crystallize mostly in two structure types, viz. the orthorhombic (space group *Immm*) W₂CoB₂ type (Rieger *et al.*, 1966) and the tetragonal (space group *P4/mbm*) Mo₂FeB₂ type (Rieger *et al.*, 1964), the latter being a ternary ordered variant of the U₃Si₂ type (Zachariasen, 1949). The distorted derivative of the U₃Si₂ type with unit-cell doubling along the *c* axis is the Zr₃Al₂ structure type (space group *P4₂/mnm*) (Wilson & Spooner, 1960). The ternary ordered variants of the Zr₃Al₂ type are the U₂Pt₂Sn (Gravereau *et al.*, 1994) and the Er₂Au₂Sn structure types (Pöttgen, 1994). An extensive review dealing with intermetallic compounds with ordered U₃Si₂ or Zr₃Al₂-type structures was published recently by Lukachuk & Pöttgen (2003). It should be noted that there are no aluminium germanides *RE₂AlGe₂* of the Mo₂FeB₂ type, while aluminium silicides *RE₂AlSi₂* and *RE₂Al₂Si*, as well as indium germanides *RE₂InGe₂*, exist. However, Choe *et al.* (2002) found another mode of atomic distribution for aluminium germanides that is realised in the new monoclinic structure type Gd₂AlGe₂. Quite recently, Rodewald *et al.* (2006) reported a new superstructure of the Mo₂FeB₂ type, viz. a tetragonal phase (space group *P4/m*) with composition Er_{2.30}Ni_{1.84}In_{0.70}.

The *RE₂T₂X* and *RE₂X'₂X* phases have received special attention for their outstanding physical properties. A precise determination of the crystal structure for phases of these compositions is a basic requirement for the better understanding of their physical properties. During systematic investigation of the Dy–Al–Ge system (Kuprysyuk, 2005), it was established that the compound Dy₂AlGe₂ forms neither as a cast alloy nor when annealed at 873 K. The alloy with nominal composition Dy₄₀Al₂₀Ge₄₀ was found to consist of three different phases, namely of DyAlGe, Dy₂AlGe₃ and Dy₅Ge₃. The new compound, namely Dy₂AlGe₂, was obtained during systematic investigation of the quaternary system Dy–

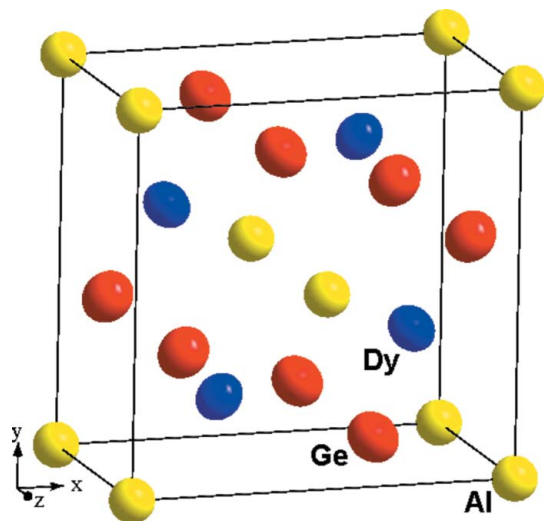


Figure 1
A clinographic projection of the Dy_2AlGe_2 unit cell, with displacement ellipsoids drawn at the 95% probability level.

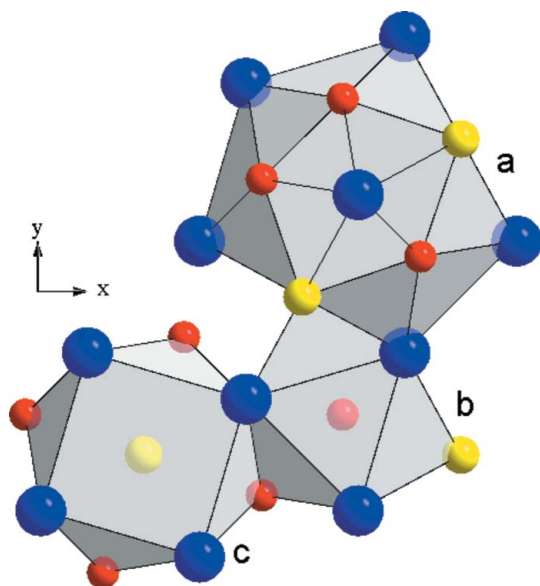


Figure 2
The coordination polyhedra around (a) the Dy atom, (b) the Ge atom and (c) the Al atoms. Key: Dy atoms are blue, Ge atoms are red and Al atoms are yellow.

Ni–Al–Ge, and we present here the results of a single-crystal structure study.

Dy_2AlGe_2 adopts the Mo_2FeB_2 structure type (Rieger *et al.*, 1964). A clinographic projection of the unit cell is shown in Fig. 1. The coordination sphere around Dy (site symmetry $m.2m$) consists of 17 atoms, if bonding interactions are considered for distances $< 4.3 \text{ \AA}$, resulting in a distorted pentagonal prism with seven additional capping atoms, $[\text{DyGe}_6\text{Al}_4\text{Dy}_7]$ (Fig. 2a). The bases of the prism have the composition $[\text{Ge}_3\text{Al}_2]$ and five additional Dy atoms cap the faces of the prism, while two other Dy atoms cap the bases of the prism at a distance of $4.291(3) \text{ \AA}$. The coordination polyhedron for Ge (site symmetry $m.2m$; bonding interactions $< 3.1 \text{ \AA}$) is a deformed (ratio height/width = 1.17) triangu-

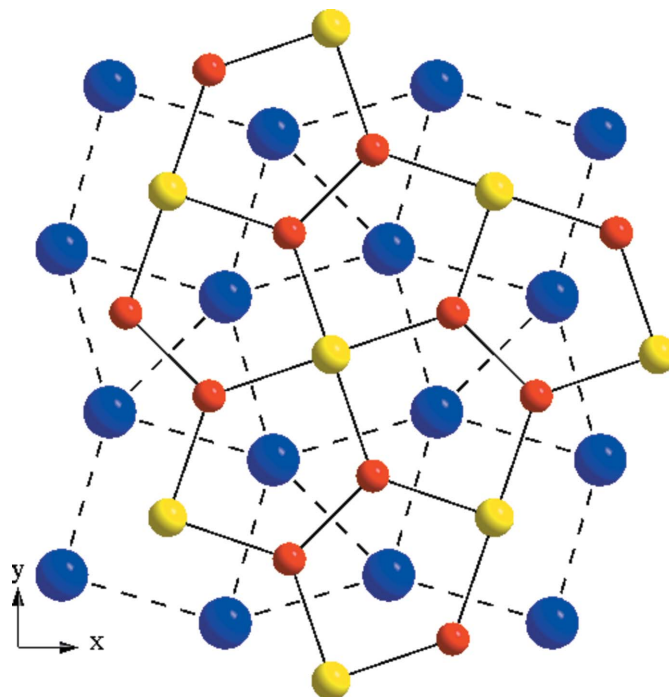


Figure 3
The networks in the structure of Dy_2AlGe_2 . The solid lines show the pentagonal $[\text{Ge}_2\text{Al}]$ network at $z = 0$ and the dashed lines show the 43^243 network of Dy atoms at $z = 0.5$. Dy atoms are blue, Ge atoms are red and Al atoms are yellow.

mented trigonal prism $[\text{GeGeAl}_2\text{Dy}_6]$ with two $[\text{Dy}_3]$ bases and two Al and one Ge as capping atoms (Fig. 2b). The Al atom (site symmetry $4/m..$; bonding interactions $< 3.4 \text{ \AA}$) centres a tetragonal prism $[\text{AlGe}_4\text{Dy}_8]$ with two $[\text{Dy}_4]$ bases and four additional Ge as capping atoms (Fig. 2c). The structure of Dy_2AlGe_2 adopts class #10 (coordination number $6 + n$ for the smallest atom ($n = 0-5$), a trigonal prism and its derivatives as coordination polyhedron) according to the classification scheme of Kryptayevich (1977).

Dy_2AlGe_2 belongs to the family of two-layer structures, like more than 70 other inorganic structure types that are listed in the structure type compilation TYPIX (Parthé *et al.*, 1993–1994). The first layer at $z = 0$ consists of a pentagonal network $[\text{Ge}_2\text{Al}]$, and the second layer at $z = 0.5$ consists of a 43^243 network of Dy atoms (Fig. 3). The structure of Dy_2AlGe_2 can alternatively be described as an intergrowth of distorted CsCl and AlB_2 -related slabs of compositions DyAl and DyGe_2 , respectively. However, slabs with exactly the same compositions and the same structures do not exist as binary phases.

The interatomic distances (Table 1) are in good agreement with the sums of the atomic radii (Emsley, 1991). The shortest distance with the highest deviation (96.5% of the sum of the atomic radii) is observed between Dy and Ge atoms, with a Dy–Ge distance of $2.896(2) \text{ \AA}$, which indicates partial covalent bonding.

Experimental

The single crystal used in this work was extracted from a cast alloy of nominal composition $\text{Dy}_{25}\text{Ni}_{25}\text{Al}_{30}\text{Ge}_{20}$, which was prepared by arc

melting of the elements (purity for Ni, Al and Ge better than 99.9%, and 99.84% for Dy) in an electric arc furnace with a water-cooled copper bottom under an Ar atmosphere (Ti-getter). A preliminary crystal investigation was performed using Laue and rotation methods (RKV-86 and RGNS-2 chambers, Mo $K\alpha$ radiation). The chemical composition of the crystal was determined with an energy-dispersive X-ray spectrometer PV9800 using a standardless procedure. The results of the energy dispersive X-ray (EDX) analysis (in atomic %) are: Dy 39.06, Ni 0.39, Al 26.10, Ge 34.45, with a precision of 2%. These values are close to the composition obtained from the structural refinement. No other impurities were found. According to the EDX spectra, the investigated single crystal contains a very small amount of Ni, close to the detection limit. We performed an X-ray powder analysis ('DRON-4.13' powder diffractometer) of the sample with nominal composition $\text{Dy}_{40}\text{Ni}_6\text{Ge}_{34}\text{Al}_{20}$, prepared as a cast alloy and as an alloy annealed at 873 K. However, the phase Dy_2AlGe_2 was not detected. Therefore, we assume that the title compound forms only as single crystals, stabilized by very small amounts of Ni, or exists in a narrow temperature region.

Crystal data

Dy_2AlGe_2	Mo $K\alpha$ radiation
$M_r = 497.16$	Cell parameters from 706 reflections
Tetragonal, $P4/mbm$	$\theta = 4.8\text{--}33.2^\circ$
$a = 7.019$ (3) Å	$\mu = 48.99\text{ mm}^{-1}$
$c = 4.291$ (3) Å	$T = 295$ (2) K
$V = 211.4$ (2) Å ³	Elongated prism, metallic light grey
$Z = 2$	$0.13 \times 0.05 \times 0.03\text{ mm}$
$D_x = 7.809\text{ Mg m}^{-3}$	

Data collection

Oxford Diffraction Xcalibur3 CCD diffractometer	248 independent reflections
ω scans	238 reflections with $I > 2\sigma(I)$
Absorption correction: analytical (<i>CrysAlis RED</i> ; Oxford Diffraction, 2005)	$R_{\text{int}} = 0.071$
$T_{\text{min}} = 0.057$, $T_{\text{max}} = 0.292$	$\theta_{\text{max}} = 33.2^\circ$
1833 measured reflections	$h = -10 \rightarrow 10$
	$k = -10 \rightarrow 9$
	$l = -6 \rightarrow 3$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0073P)^2 + 11.6525P]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.082$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.31$	$\Delta\rho_{\text{max}} = 2.20\text{ e \AA}^{-3}$
248 reflections	$\Delta\rho_{\text{min}} = -3.04\text{ e \AA}^{-3}$
12 parameters	Extinction correction: <i>SHELXL97</i>
	Extinction coefficient: 0.0029 (8)

Table 1

Selected bond lengths (Å).

Dy—Ge ⁱ	2.896 (2)	Dy—Dy ^v	3.6578 (18)
Dy—Ge ⁱⁱ	3.0460 (16)	Ge—Ge ^{vi}	2.531 (4)
Dy—Al ⁱⁱⁱ	3.3605 (14)	Ge—Al ^{vii}	2.7638 (16)
Dy—Dy ^{iv}	3.507 (2)		

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

Analysis of the systematic absences using the program *ABSEN* (McArdle, 1996) led to the extinction symbol P - b - and possible space groups $P\bar{4}b2$, $P4bm$ and centrosymmetric $P4/mbm$. A statistical test

of the distribution of the E values, using the program *E-STATS* from the *WinGX* system (Farrugia, 1999), suggested that the structure is centrosymmetric with a probability of 70%. Taking into account some notes on choosing a centre of symmetry (Marsh, 1995), the structure solution and refinement were also performed in the non-centrosymmetric space groups $P\bar{4}b2$ and $P4bm$, and in space groups $P4/m$ (as a model of the $\text{Er}_{2.30}\text{Ni}_{1.84}\text{In}_{0.70}$ structure type), $P4_2/mmm$ (as a model of the ordered Zr_3Al_2 structure type) and $Pbam$ (as a subgroup of $P4/mbm$). The structure refinement of Dy_2AlGe_2 clearly indicates that this phase crystallizes in the centrosymmetric space group $P4/mbm$, since solution and refinements in the other space groups were less satisfactory and resulted in higher R factors and atomic displacement parameters. Attempts to refine some variants of statistical atomic distribution in order to adjust the composition determined from EDX spectra, including incorporation of Ni, failed. The atomic coordinates were standardized using the program *STRUCTURE_TIDY* (Gelato & Parthé, 1987). The highest maximum residual electron density is 0.84 \AA^{-3} from Al and the deepest hole is 1.99 \AA^{-3} from Ge.

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*.

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