Dy$_2$Ni$_7$Sn$_3$: a new member of the CaCu$_5$ family of intermetallics

V. Romaka,[a]* R. Gladyshevskii,[a] B. Marciniak[b] and V. Pavlyuk[a]

[a]Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya Str. 6, 79005 Lviv, Ukraine, and [b]Jan Dlugosz University of Czestochowa, Institute of Chemistry and Environmental Protection, al. Armii Krajowej 13/15, 42200 Czestochowa, Poland

Correspondence e-mail: romakav@yahoo.com

Single crystals of didysprosium heptanickel tritin were synthesized from the constituent elements by arc-melting. Two of the five Ni atoms are at general sites and all other atoms are at sites with either twofold or m symmetry. The structure contains 'DyNi$_5$Sn' and 'DyNi$_2$Sn$_2$' fragments and represents a new member of the CaCu$_5$ series of intermetallics.

Comment

Investigation of the Dy–Ni–Sn ternary system revealed the presence of a large number of Ni-enriched compounds (Romaka *et al.*, 2007), including a new stannide with the composition Dy$_{18}$Ni$_{55}$Sn$_{27}$. After the structure of this new stannide had been solved and refined, the crystal chemistry analysis was carried out. Interatomic distances (Table 1) in the structure are in good agreement with the sum of the corresponding atomic radii. No shortening of the interatomic distances between Sn atoms caused by covalent bonding (inherent in compounds with high Sn content) was observed. Most ternary intermetallics are constructed from fragments of the most stable binary compounds and the structure analysis of already known Ni-enriched stannides shows that all are derived from the binary DyNi$_5$ compound, which crystallizes in the CaCu$_5$ structure type (Wernick & Geller, 1959). The crystal structure of Dy$_2$Ni$_7$Sn$_3$ (Fig. 1a) belongs to the CaCu$_5$ family and contains 'DyNi$_5$Sn' (denoted I) and 'DyNi$_2$Sn$_2$' (denoted II) fragments (Fig. 1b). The 'DyNi$_5$Sn' fragment seems to be very similar to that in DyNi$_5$Sn (Skolozdra *et al.*, 1996), but with a different position for one inner Ni atom. In other respects, both fragments are similar. The 'DyNi$_2$Sn$_2$' fragment is a hypothetical structure because there is no compound with this stoichiometry in the Dy–Ni–Sn system. However, this fragment resembles the deformed fragment in the YB$_2$C$_2$ structure (Bauer & Nowotny, 1971). Stacking of the 'DyNi$_5$Sn' and 'DyNi$_2$Sn$_2$' fragments in the sequence I–II–I′–I–II–I′ may produce the structure of Dy$_2$Ni$_7$Sn$_3$ (Fig. 1b). The

main feature of this compound is the manner of stacking of the 'DyNi$_5$Sn' and 'DyNi$_2$Sn$_2$' fragments. There is no possibility of building fragment I directly from the previous fragment (I′) because the shared sides of these fragments are shifted and stacked along the Dy plane (Fig. 1b).

By analyzing the Ni-enriched DyNi$_5$Sn, Dy$_2$Ni$_7$Sn$_3$ and DyNi$_3$Sn$_2$ (Skolozdra *et al.*, 1988) ternary stannides of the Dy–Ni–Sn system, it was found that all of them were derived from
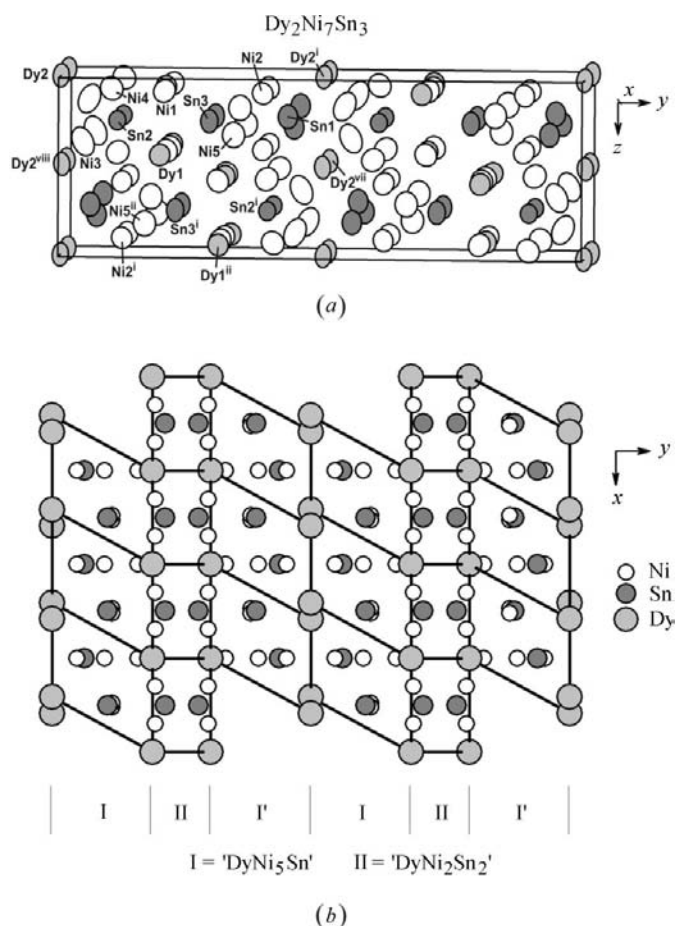

Figure 1
(a) The unit cell of the title compound, with displacement ellipsoids drawn at the 95% probability level and (b) the stacked fragments in the Dy$_2$Ni$_7$Sn$_3$ structure. [Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (ii) $-x, \frac{1}{2} - y, -\frac{1}{2} + z$; (vii) $-x, -y + \frac{1}{2}, z + \frac{1}{2}$; (viii) $-x + \frac{1}{2}, -y, z + \frac{1}{2}$.]
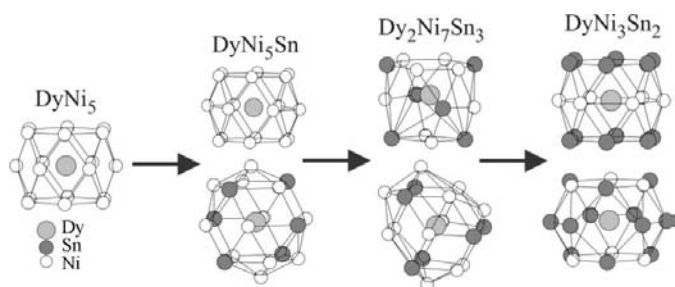

Figure 2
The structure relationships of the Dy polyhedra in the DyNi$_5$–DyNi$_5$Sn–Dy$_2$Ni$_7$Sn$_3$–DyNi$_3$Sn$_2$ series.

inorganic compounds

the binary $DyNi_5$ genetic prototype. Structure relationships between these compounds are shown in Fig. 2. While advancing from binary $DyNi_5$ to ternary $DyNi_5Sn$, the coordination polyhedron of the Dy atom splits into two different polyhedra: one replicates that of the binary compound and the other is slightly deformed, but still very similar to that in the $DyNi_5$ compound. Passing through $DyNi_5Sn$ to $Dy_2Ni_7Sn_3$, the polyhedra for the Dy atoms become deformed, but the motif of the $DyNi_5$ fragment can be easily recognized. The Dy polyhedra of the last stannide, $DyNi_3Sn_2$, are almost analogous to the initial Dy polyhedron in the $DyNi_5$ compound.

Experimental

A sample with nominal composition $Dy_{18}Ni_{55}Sn_{27}$ was prepared by arc-melting the component Dy (99.9 wt.%), Ni (99.99 wt.%) and Sn (99.999 wt.%) metals on a water-cooled copper hearth under a protective Ti-gettered argon atmosphere. The obtained alloy was annealed at 870 K for 720 h in an evacuated silica ampoule and finally quenched in cold water. A crystal of $Dy_2Ni_7Sn_3$ suitable for single-crystal X-ray diffraction analysis was extracted directly from the annealed sample. The chemical composition of the crystal was determined *via* EDX (energy dispersive X-ray) analysis on a Carl Zeiss DSM 962 scanning electron microscope equipped with a Link EDX system, giving 18.2 (1)% Dy, 55.5 (3)% Ni, and 26.3 (2)% Sn. These values are very close to the composition calculated from the structure refinement.

Crystal data

$Dy_2Ni_7Sn_3$	$V = 1532.02\ (7)$ Å^3
$M_r = 1092.04$	$Z = 8$
Orthorhombic, $Cmca$	Mo $K\alpha$ radiation
$a = 8.5964\ (2)$ Å	$\mu = 45.49$ mm^{-1}
$b = 23.6415\ (6)$ Å	$T = 298\ (2)$ K
$c = 7.5383\ (2)$ Å	$0.30 \times 0.20 \times 0.17$ mm

Data collection

Oxford Diffraction Xcalibur diffractometer with a CCD detector	6228 measured reflections
	1232 independent reflections
	1033 reflections with $I > 2\sigma(I)$
Absorption correction: analytical (de Meulenaer & Tompa, 1965)	$R_{int} = 0.034$
$T_{min} = 0.040$, $T_{max} = 0.143$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$	65 parameters
$wR(F^2) = 0.067$	$\Delta\rho_{max} = 2.63$ e Å^{-3}
$S = 1.24$	$\Delta\rho_{min} = -3.04$ e Å^{-3}
1232 reflections	

The structure solution and refinement were also performed in the noncentrosymmetric space group $C2ce$ but were less satisfactory and resulted in larger R indices and atomic displacement parameters.

Table 1
Selected bond lengths (Å).

Ni1—Sn3	2.5107 (14)	Ni2—Dy1^{ii}	3.0258 (13)
Ni1—Ni2^{i}	2.5207 (17)	Ni3—Ni4	2.587 (2)
Ni1—Ni5^{ii}	2.5277 (19)	Ni3—Sn1^{vi}	2.616 (2)
Ni1—Ni1^{iii}	2.606 (2)	Ni3—Sn1^{vii}	2.672 (2)
Ni1—Ni4	2.6435 (19)	Ni3—Sn2	2.6849 (11)
Ni1—Sn3^{i}	2.6533 (12)	Ni3—Dy2^{viii}	2.9657 (10)
Ni1—Sn2	2.6707 (14)	Ni3—Dy2	3.3986 (16)
Ni1—Dy1	2.9332 (13)	Ni4—Ni5^{ii}	2.396 (2)
Ni1—Dy1^{iv}	2.9974 (12)	Ni4—Sn2	2.5990 (10)
Ni1—Dy1^{ii}	3.0792 (13)	Ni4—Sn1^{ii}	2.8050 (19)
Ni2—Ni2^{v}	2.385 (2)	Ni4—Dy2	3.0171 (14)
Ni2—Ni4^{i}	2.5360 (14)	Dy1—Ni5^{vii}	2.9698 (19)
Ni2—Sn1	2.5656 (13)	Dy1—Sn2	3.2630 (7)
Ni2—Sn2^{i}	2.5921 (12)	Dy1—Sn3	3.2791 (7)
Ni2—Ni5^{iv}	2.6381 (15)	Ni5—Sn3	2.5213 (10)
Ni2—Sn3	2.6868 (13)	Ni5—Sn1	2.5733 (19)
Ni2—Dy2^{i}	2.8676 (12)	Sn1—Dy2^{vii}	3.1942 (8)
Ni2—Ni5	2.8758 (17)	Sn1—Dy2^{i}	3.3016 (7)
Ni2—Sn1^{iv}	3.0002 (13)	Sn2—Dy2	3.1667 (6)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

References

Bauer, J. & Nowotny, H. (1971). *Monatsh. Chem.* **102**, 1129–1145.
Brandenburg, K. (1999). *DIAMOND*. Version 2.1e. Crystal Impact GbR, Bonn, Germany.
Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.
Oxford Diffraction (2005). *CrysAlis RED* and *CrysAlis CCD*. Versions 1.171.29.2. Oxford Diffraction Poland, Wrocław, Poland.
Romaka, V. V., Gladyshevskii, R. E. & Tkachuk, A. V. (2007). 10th International Conference on Crystal Chemistry of Intermetallic Compounds, Collected Abstracts, p. 36.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Skolozdra, R., Szymczak, R., Szymczak, H., Romaka, L. & Baran, M. (1996). *J. Phys. Chem. Solids*, **57**, 357–363.
Skolozdra, R. V., Komarovskaya, L. P. & Akselrud, L. G. (1988). *Izv. Akad. Nauk. SSSR Neorg. Mater.* **24**, 1490–1493.
Wernick, J. H. & Geller, S. (1959). *Acta Cryst.* **12**, 662–665.