

**Er<sub>5</sub>Ni<sub>3</sub>Al<sub>3</sub>Ge<sub>4</sub>: a quaternary variant of the NbCoB type**Pavlo Demchenko,<sup>a\*</sup> Joanna Kończyk,<sup>b</sup> Grigori Demchenko,<sup>a</sup> Roman Gladyshevskii<sup>a</sup> and Volodymyr Pavlyuk<sup>a</sup><sup>a</sup>Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine, and <sup>b</sup>Institute of Chemistry and Environment Protection, Jan Dlugosz University, al. Armii Krajowej 13/15, 42-200 Czestochowa, Poland

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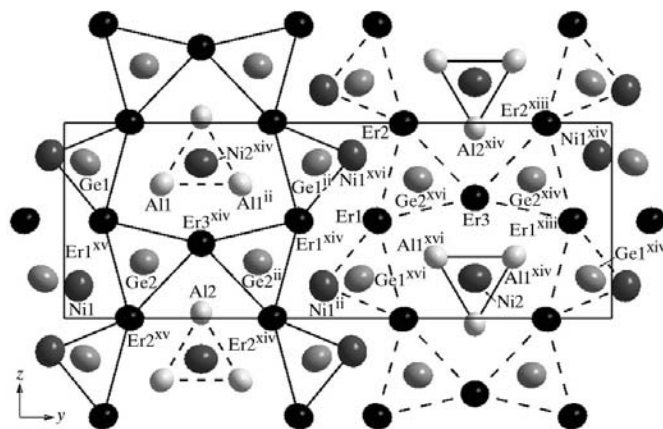
Single crystals of pentaerbium trinickel trialuminium tetra-germanium were synthesized from the elements by arc-melting. The novel compound crystallizes in the space group *Pmmn*, *e*<sup>6</sup>*b*<sup>2</sup>*a*, with all nine crystallographically unique atoms in special positions of site symmetries *m.* and *mm*2. This compound represents a new ordered variant of the NbCoB type. Its two-layer structure is described as an intergrowth of the Er<sub>3</sub>NiAl<sub>3</sub>Ge<sub>2</sub> (Y<sub>3</sub>NiAl<sub>3</sub>Ge<sub>2</sub> type) and ErNiGe (TiNiSi type) structures. The coordination polyhedra are distorted pentagonal prisms around Er atoms, tetragonal prisms around Al and Ni atoms, and trigonal prisms around Ge and Ni atoms, capped with eight, four and three extra vertices, respectively.

**Comment**

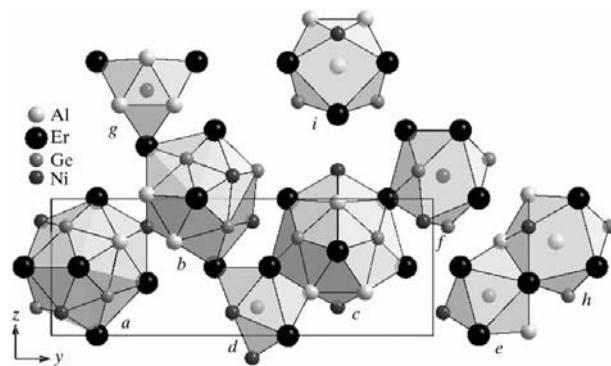
Rare-earth intermetallics of different compositions have received attention because of their interesting and useful physical properties, such as the co-existence of superconductivity and magnetism, the Kondo effect, and the magnetocaloric effect. The search for new intermetallic phases is necessary for the development of new materials, and the accurate determination of their crystal structures is the basic requirement for a better understanding of their physical properties. The NbCoB structure type was discovered by Krypyakevich *et al.* (1971). Since then, only one other representative, TaCoB (Kuz'ma & Rudakevich, 1973), has been found among intermetallics. Recently, Fedorchuk *et al.* (2005) reported the existence of Yb<sub>5</sub>Mg<sub>3</sub>Ga<sub>7</sub>, which represents a new type of ordering in the NbCoB structure. The title compound, Er<sub>5</sub>Ni<sub>3</sub>Al<sub>3</sub>Ge<sub>4</sub>, which is yet another quaternary variant of the NbCoB type, was obtained during a systematic investigation of the Er–Ni–Al–Ge system. We present here the results of a single-crystal structure study.

A projection of the Er<sub>5</sub>Ni<sub>3</sub>Al<sub>3</sub>Ge<sub>4</sub> unit cell on to the (100) plane is shown in Fig. 1. The coordination polyhedra of the

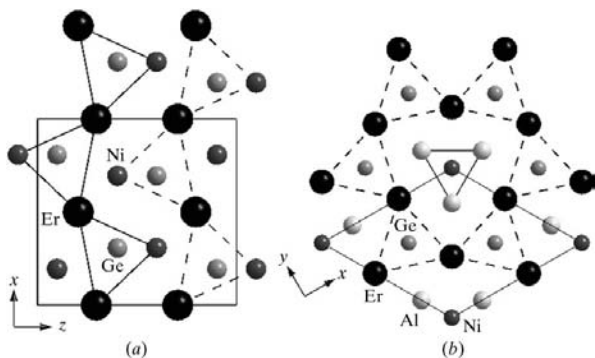
atoms are distorted pentagonal, tetragonal and trigonal prisms with eight, four and three extra vertices, as shown in Fig. 2. The coordination around atom Er1 (site symmetry *m.*) consists of 18 atoms, if bonding interactions up to 4.2 Å are included, resulting in a distorted pentagonal prism with eight additional vertices, *viz.* [Er1Ge<sub>5</sub>Ni<sub>4</sub>Al<sub>2</sub>Er<sub>7</sub>] (*a* in Fig. 2). The coordination polyhedra around atoms Er2 and Er3 (site symmetry *m.* and *mm*2, and bonding interactions < 4.2 Å) are similar pentagonal prisms with eight additional vertices of composition [Er2Ni<sub>4</sub>Ge<sub>5</sub>Al<sub>4</sub>Er<sub>5</sub>] (*b* in Fig. 2) and [Er3Ni<sub>2</sub>Ge<sub>4</sub>Al<sub>6</sub>Er<sub>6</sub>] (*c* in Fig. 2), respectively. The coordination polyhedra around the Ge atoms (site symmetry *m.*) are trigonal prisms (bonding interactions < 3 Å), *viz.* tricapped [Ge1Ni<sub>3</sub>AlEr<sub>5</sub>] (*d* in Fig. 2) and tricapped [Ge2NiAl<sub>2</sub>Er<sub>6</sub>] (*e* in Fig. 2). These trigonal prisms are deformed so that the height/width ratio of the prisms (*c/a*) is 1.18. Two types of prisms are observed for the Ni atoms. Atom Ni1 (site symmetry *m.* and bonding interactions < 3.3 Å) centres a deformed tetragonal prism, [Ni1Ge<sub>4</sub>Er<sub>6</sub>Ni<sub>2</sub>] (*f* in Fig. 2). The coordination polyhedron for atom Ni2 (site symmetry *mm*2 and bonding interactions < 3 Å) is a deformed (*c/a* = 1.54) trigonal prism, [Ni2Al<sub>6</sub>Er<sub>3</sub>] (*g* in Fig. 2). The coordination polyhedra around the Al atoms

**Figure 1**

A projection of the unit cell on to the (100) plane, with displacement ellipsoids drawn at the 95% probability level. [Symmetry codes: (ii)  $-x + \frac{1}{2}, -y + \frac{1}{2}, z$ ; (xiii)  $-x + \frac{1}{2}, -y + \frac{3}{2}, z$ ; (xiv)  $x + \frac{1}{2}, -y + 1, -z + 1$ ; (xv)  $-x + 1, y - \frac{1}{2}, -z + 1$ ; (xvi)  $-x + 1, y + \frac{1}{2}, -z + 1$ .]

**Figure 2**

The coordination polyhedra around Er1–Er3 (*a*, *b* and *c*), Ge1 and Ge2 (*d* and *e*), Ni1 and Ni2 (*f* and *g*), and Al1 and Al2 (*h* and *i*) in the Er<sub>5</sub>Ni<sub>3</sub>Al<sub>3</sub>Ge<sub>4</sub> structure



**Figure 3** Intergrowth fragments of (a) ErNiGe and (b) Er<sub>3</sub>NiAl<sub>3</sub>Ge<sub>2</sub>. The broken and solid lines correspond to the lower and upper layers, respectively.

(site symmetry *m.* for Al1 and *mm2* for Al2) are deformed tetragonal prisms (bonding interactions < 3.3 Å), viz. tetra-capped [Al1Ni<sub>2</sub>Al<sub>2</sub>Ge<sub>2</sub>Er<sub>6</sub>] (*h* in Fig. 2) and [Al<sub>2</sub>Ni<sub>2</sub>Ge<sub>2</sub>Al<sub>2</sub>Er<sub>6</sub>] (*i* in Fig. 2). These deformed tetragonal prisms centered by Al and Ni1 may also be considered as distorted cuboctahedra. The structure of Er<sub>5</sub>Ni<sub>3</sub>Al<sub>3</sub>Ge<sub>4</sub> belongs to class #10 [coordination number 6 + *n* (*n* = 0–5) for the smallest atom, a trigonal prism and its derivatives as coordination polyhedron] according to the classification scheme of Krypyakevich (1977).

The interatomic distances (Table 1) are in good agreement with the sums of the atomic radii (Emsley, 1991). The shortest Er3–Ni2 [2.798 (4) Å, 93.2% of the sum of the atomic radii] and Al1–Al2 [2.716 (6) Å, 94.9% of twice the Al atomic radius] distances indicate partial covalent bonding.

As stated above, Er<sub>5</sub>Ni<sub>3</sub>Al<sub>3</sub>Ge<sub>4</sub> is a quaternary ordered variant of the NbCoB type (Krypyakevich *et al.*, 1971); the Er atoms substitute for Nb, the Ge and Ni2 atoms substitute for B, and the Al and Ni1 atoms substitute for Co. ErNiGe (Fig. 3a) adopts the TiNiSi structure type (Gorelenko *et al.*, 1984; Brink Shoemaker & Shoemaker, 1965) and Er<sub>3</sub>NiAl<sub>3</sub>Ge<sub>2</sub> (Fig. 3b) adopts the Y<sub>3</sub>NiAl<sub>3</sub>Ge<sub>2</sub> structure type (Demchenko *et al.*, 2005; Zhao & Parthé, 1990). Er<sub>5</sub>Ni<sub>3</sub>Al<sub>3</sub>Ge<sub>4</sub> can be described as a 1:1 intergrowth of fragments of the [Er<sub>2</sub>Ni<sub>2</sub>Ge<sub>2</sub>] and [Er<sub>3</sub>NiAl<sub>3</sub>Ge<sub>2</sub>] structures. The feature common to these three structures is a puckered sheet of edge-connected columns of trigonal prisms. Er<sub>5</sub>Ni<sub>3</sub>Al<sub>3</sub>Ge<sub>4</sub> belongs to a family of two-layer compounds. More than 70 other inorganic structure types belong to this family according to the compilation in *TYPIX* (Parthé *et al.*, 1993–1994).

**Experimental**

The single crystal used in this work was extracted from an alloy of nominal composition Er<sub>25</sub>Ni<sub>25</sub>Al<sub>30</sub>Ge<sub>20</sub>. The alloy was prepared by arc-melting the elements (purity greater than 99.9% for Ni, Al and Ge, and 99.84% for Er) in an electric arc furnace with a water-cooled copper hearth under an argon atmosphere with a Ti-getter. The alloy was then annealed in an evacuated silica tube at 870 K for 350 h. A preliminary crystal investigation was performed using Laue and rotation methods (RKV-86 and RGNS-2 chambers, Mo Kα radiation). The chemical composition of the crystal was determined with an energy dispersive PV9800 X-ray spectrometer using a standardless procedure. The result of the EDX analysis is 36.47% Er, 19.72% Ni,

17.32% Al and 26.50% Ge (in atom%, with an accuracy of 2%). These values are very close to the composition obtained from the structural refinement. No impurities were found.

*Crystal data*

Er<sub>5</sub>Ni<sub>3</sub>Al<sub>3</sub>Ge<sub>4</sub>  
*M<sub>r</sub>* = 1383.73  
 Orthorhombic, *Pmmn*  
*a* = 4.1561 (6) Å  
*b* = 19.069 (1) Å  
*c* = 6.8369 (5) Å  
*V* = 541.84 (9) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 8.481 Mg m<sup>-3</sup>

Cu Kα radiation  
 Cell parameters from 18 reflections  
 θ = 15–33°  
 μ = 87.55 mm<sup>-1</sup>  
*T* = 295 (2) K  
 Elongated prism, metallic dark grey  
 0.11 × 0.02 × 0.01 mm

*Data collection*

Kuma KM-4 diffractometer  
 ω–2θ scans  
 Absorption correction: for a cylinder mounted on the φ axis (Dwiggins, 1975)  
*T<sub>min</sub>* = 0.169, *T<sub>max</sub>* = 0.382  
 3581 measured reflections  
 580 independent reflections  
 501 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.085  
 θ<sub>max</sub> = 68.0°  
*h* = –5 → 4  
*k* = –22 → 14  
*l* = –8 → 8  
 3 standard reflections every 100 reflections  
 intensity decay: 2%

*Refinement*

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.043  
*wR* (*F*<sup>2</sup>) = 0.111  
*S* = 1.16  
 580 reflections  
 50 parameters

*w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (0.0783*P*)<sup>2</sup> + 0.734*P*]  
 where *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> = 0.001  
 Δρ<sub>max</sub> = 3.99 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = –2.75 e Å<sup>-3</sup>  
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.00070 (11)

**Table 1**

Selected bond lengths (Å).

Er1–Ge2 <sup>i</sup>	2.9027 (13)	Er2–Ge1 <sup>ii</sup>	3.314 (2)
Er1–Ge1 <sup>ii</sup>	2.9215 (18)	Er2–Er3	3.6020 (12)
Er1–Ni1 <sup>iii</sup>	2.942 (3)	Er3–Ni2	2.798 (4)
Er1–Ge1 <sup>iii</sup>	2.9690 (14)	Er3–Ge2 <sup>x</sup>	2.9433 (12)
Er1–Al1 <sup>i</sup>	3.173 (3)	Er3–Al2 <sup>x</sup>	3.198 (5)
Er1–Ni1 <sup>i</sup>	3.207 (2)	Er3–Al1 <sup>iii</sup>	3.227 (3)
Er1–Er1 <sup>iv</sup>	3.4299 (15)	Ge1–Ni1 <sup>vi</sup>	2.4293 (18)
Er1–Er3	3.4940 (9)	Ge1–Ni1 <sup>vi</sup>	2.540 (3)
Er1–Er2	3.5180 (10)	Ge1–Al1	2.771 (4)
Er1–Er2 <sup>v</sup>	3.5593 (10)	Ge2–Ni1	2.442 (3)
Er2–Ni2 <sup>vi</sup>	2.873 (2)	Ge2–Al2	2.663 (4)
Er2–Ge2 <sup>iii</sup>	2.8971 (12)	Er2–Al1	2.777 (4)
Er2–Ge1 <sup>vii</sup>	2.9475 (13)	Ni2–Al1 <sup>x</sup>	2.594 (3)
Er2–Ni1 <sup>iii</sup>	2.9576 (19)	Ni2–Al2 <sup>xii</sup>	2.627 (4)
Er2–Ni1 <sup>viii</sup>	3.005 (3)	Al1–Al2 <sup>vi</sup>	2.716 (6)
Er2–Al1 <sup>ix</sup>	3.212 (3)	Al1–Al1 <sup>ii</sup>	2.729 (8)
Er2–Al2 <sup>x</sup>	3.2467 (8)		

Symmetry codes: (i) *x* + ½, *y* + ½, –*z* + 1; (ii) –*x* + ½, –*y* + ½, *z*; (iii) *x* – ½, *y* + ½, –*z* + 1; (iv) –*x*, –*y* + 1, –*z* + 1; (v) *x*, *y*, *z* – 1; (vi) *x*, *y*, *z* + 1; (vii) *x* – ½, *y* + ½, –*z* + 2; (viii) –*x* + ½, –*y* + ½, *z* + 1; (ix) *x* + ½, *y* + ½, –*z* + 2; (x) –*x* + 1, –*y* + 1, –*z* + 1; (xi) –*x*, –*y*, –*z* + 1; (xii) –*x*, –*y* + 1, –*z*.

The analysis of the systematic absences using the program *ABSEN* (McArdle, 1996) led to the extinction symbol *P*–*n* and possible space groups *Pm2<sub>1</sub>n*, *P2<sub>1</sub>mn* and centrosymmetric *Pmmn*. 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 80%. 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 group. The results clearly indicated that Er<sub>5</sub>Ni<sub>3</sub>Al<sub>3</sub>Ge<sub>4</sub> crystallizes in the centrosymmetric space group *Pmmn*, since the solution and refinement in the non-centrosymmetric variants were less satis-

factory and resulted in larger  $R$  indices and atomic displacement parameters. The atomic coordinates were standardized using the *STRUCTURE TIDY* program (Gelato & Parthé, 1987). The highest residual electron-density peak is 0.97 Å from atom Er3 and the deepest hole is 0.95 Å from atom Er2.

Data collection: *KM4B8 Software* (Galdecki *et al.*, 1996); cell refinement: *KM4B8 Software*; data reduction: *KM4B8 Software*; 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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1097). Services for accessing these data are described at the back of the journal.

## References

- Brandenburg, K. (1999). *DIAMOND*. Version 2.1e. Crystal Impact GbR, Bonn, Germany.
- Brink Shoemaker, C. & Shoemaker, D. P. (1965). *Acta Cryst.* **18**, 900–905.
- Demchenko, G., Kończyk, J., Demchenko, P., Bodak, O. & Marciniak, B. (2005). *Acta Cryst.* **E61**, i273–i274.
- Dwiggins, C. W. Jr (1975). *Acta Cryst.* **A31**, 146–148.
- Emsley, J. (1991). *The Elements*, 2nd ed. Oxford: Clarendon Press.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Fedorchuk, A. O., Prots, Yu., Schnelle, W., Schmidt, M. & Grin, Yu. (2005). *Gemeinsame Jahrestagung der DGK, DGKK und NKK-ÖAW, Köln*, in *Referate*, p. 177. München: Oldenbourg Verlag.
- Galdecki, Z., Kowalski, A., Kucharczyk, D. & Uszynski, I. (1996). *KM4B8 Software*. Kuma Diffraction Ltd, Wrocław, Poland.
- Gelato, L. M. & Parthé, E. (1987). *J. Appl. Cryst.* **20**, 139–143.
- Gorelenko, Yu. K., Starodub, P. K., Bruskov, V. A., Skolozdra, R. V., Yarovets, V. I., Bodak, O. I. & Pecharsky, V. K. (1984). *Ukr. Fiz. Zh. Ukr. Ed.* **29**, 867–871. (In Ukrainian.)
- Krypyakevich, P. I. (1977). In *Structure Types of Intermetallic Compounds*. Moscow: Nauka. (In Russian.)
- Krypyakevich, P. I., Kuz'ma, Yu. B., Voroshilov, Yu. V., Brink Shoemaker, C. & Shoemaker, D. P. (1971). *Acta Cryst.* **B27**, 257–261.
- Kuz'ma, Yu. B. & Rudakevich, O. M. (1973). *Dopov. Akad. Nauk Ukr. RSR Ser. A*, **2**, 164–167. (In Ukrainian.)
- McArdle, P. (1996). *J. Appl. Cryst.* **29**, 306.
- Marsh, R. E. (1995). *Acta Cryst.* **B51**, 897–907.
- Parthé, E., Gelato, L., Chabot, B., Penzo, M., Cenxual, K. & Gladyshevskii, R. (1993–1994). *TYPIX – Standardized Data and Crystal Chemical Characterization of Inorganic Structure Types*, in *Gmelin Handbook of Inorganic and Organometallic Chemistry*. Heidelberg: Springer.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Zhao, J. T. & Parthé, E. (1990). *Acta Cryst.* **C46**, 2273–2276.