

A new rhombohedral modification of
EuNi₅InInna Bigun,^a Volodymyr Smetana^b and Yaroslav
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A rhombohedral modification of europium pentanickel indide, r-EuNi₅In, crystallizes in the $R\bar{3}m$ space group and adopts the UCu₅In structure type. The structure is closely related to the hexagonal, h-EuNi₅In, form (CeNi₅Sn type). Both EuNi₅In modifications are composed of CaCu₅ (EuNi₅)-, MgCu₂ (InNi₂)- and NiAs (EuNi)-type slabs in a 1:2:1 ratio. The atoms in the structure have high coordination numbers, viz. 20 and 18 for europium, 14 for indium, and 12 and 10 for nickel. The structure features a two-dimensional network of ∞^2 [Ni₈] tetrahedral clusters arranged in the *ab* plane.

Comment

Extensive investigations focused on the interaction of rare earths (RE) with transition metals and indium have clearly demonstrated that the formation of numerous intermetallic compounds is typical for RE–Ni–In systems (Kalychak *et al.*, 2004; Kalychak, 1997). More than 25 structure types have been reported for these intermetallics (Kalychak *et al.*, 2004). Besides the large structural variety, the RE_xNi_yIn_z compounds have attracted considerable interest owing to their distinctive magnetic and electrical properties, as well as their hydrogen-storage behavior. In this context, the representatives with cerium, europium and ytterbium are the most interesting. Several of these compounds show valence instabilities or unusual magnetic ordering phenomena. Rare earth intermetallics containing europium exhibit a wide range of interesting and unusual physical properties, which are mostly related to their mixed-valence nature (II/III) (Zaremba *et al.*, 2006; Pöttgen *et al.*, 1996). Unfortunately, these systems remain much less well known, which may be explained, along with other reasons, by the experimental difficulties of alloy synthesis. To date, the existence of seven compounds in the Eu–Ni–In system has been confirmed: EuNi_{7+x}In_{6-x} (LaNi₇In₆ structure type; Zaremba *et al.*, 2006), EuNi₉In₂ (YNi₉In₂ structure type; Kalychak *et al.*, 1984), EuNi₃In₆ (LaNi₃In₆ structure type; Kalychak *et al.*, 1997), EuNi₅In (CeNi₅Sn

structure type; Baranyak *et al.*, 1992), EuNiIn₄ (YNiAl₄ structure type; Kalychak *et al.*, 1988; Pöttgen *et al.*, 1996), EuNiIn₂ (MgCuAl₂ structure type; Kalychak *et al.*, 1997) and EuNi_{0.5}In_{1.5} (AlB₂ structure type; Baranyak, Dmytrakh *et al.*, 1988).

During the study of the ternary Eu–Ni–In phase diagram, the novel modification of EuNi₅In was found and its crystal structure determined by single-crystal X-ray diffraction. The compound adopts the UCu₅In (Stępień-Damm *et al.*, 1999; Hlukhyy, 2003) structure type. An orthorhombic projection of the unit cell and the coordination polyhedra of the atoms are shown in Fig. 1. Two types of polyhedra were observed for Eu1 and Eu2 atoms on Wyckoff sites 3*a* and 3*b*, namely eight-capped hexagonal [Eu1Ni₁₈In₂] prisms and six equatorially capped and two base-capped pentagonal [Eu2Ni₁₂In₆] anti-prisms. Distorted [Ni1Ni₉Eu₃] and [Ni3Ni₇In₂Eu₃] icosahedra are filled by Ni1 and Ni3 atoms, respectively, and Ni2 has ten-vertex [Ni2Ni₃In₄Eu₃] polyhedra. The In atoms are located at the centers of [InNi₁₀Eu₄] polyhedra.

EuNi₅In is a nickel-rich compound. Three crystallographically different nickel sites, with Ni–Ni distances ranging from 2.4330 (15) to 2.4784 (16) Å, can be found within the rhombohedral EuNi₅In (r-EuNi₅In) structure. Compared to the Ni–Ni distance of 2.49 Å in the face-centered cubic (f.c.c.) structure of nickel (Donohue, 1974), we can assume a significant degree of Ni–Ni bonding. Here, the central

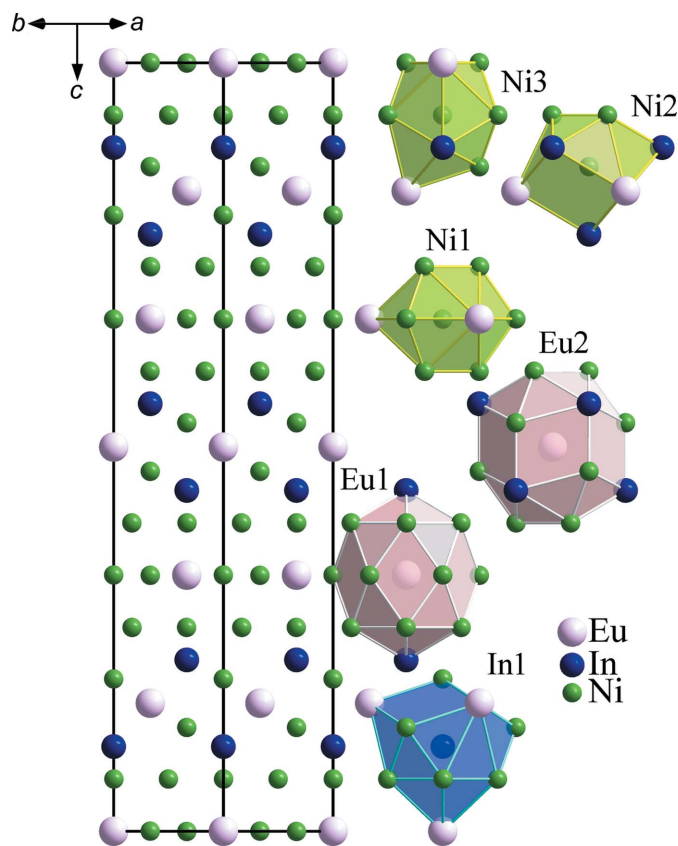
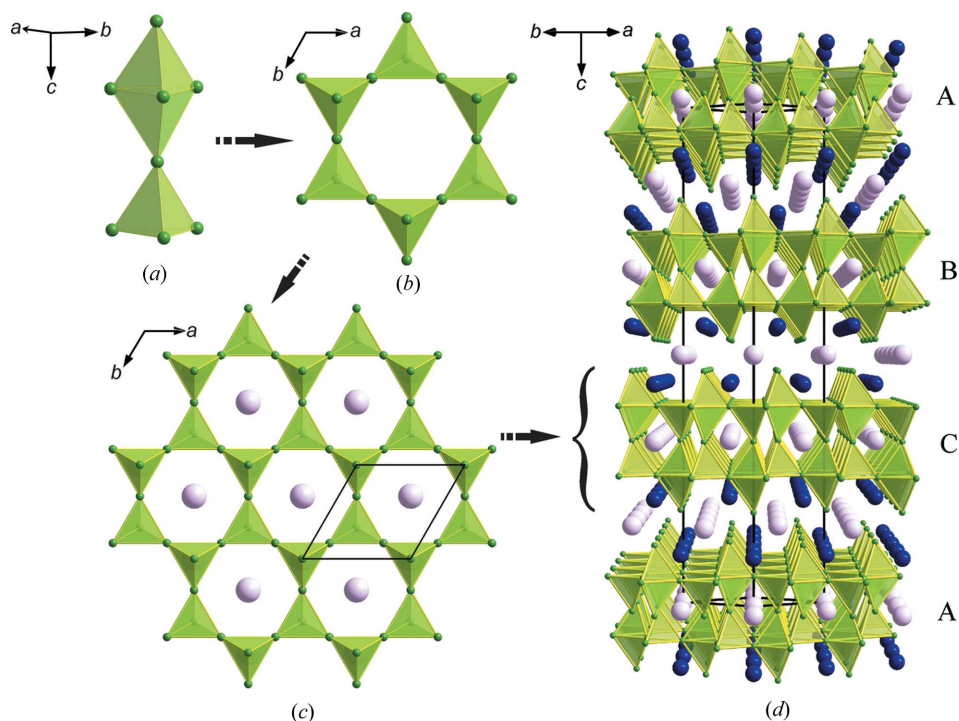


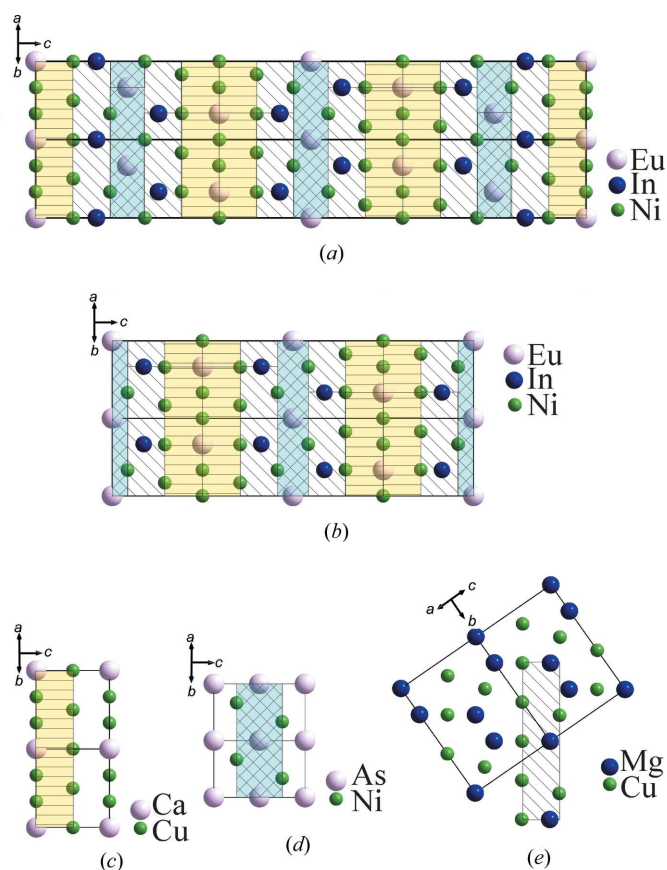
Figure 1
A projection of the EuNi₅In unit cell in an orthorhombic aspect and a view of the coordination polyhedra of the atoms. Generic atom labels without consideration of symmetry operators are used.

**Figure 2**

(a) The $[\text{Ni}_8]$ tetrahedral unit; (b) the hexagonal ring of six $[\text{Ni}_8]$ units; (c) the ${}^2_\infty[\text{Ni}_8]$ two-dimensional layer; (d) the ABC sequence of ${}^2_\infty[\text{Ni}_8]$ layers in the EuNi_5In structure.

building unit is a distorted tetrahedron formed by three Ni3 atoms in the $18h$ position and one Ni1 or Ni2 atom, both occupying the $6c$ sites. The tetrahedra now alternately share vertices and faces along the c axis, thereby forming an $[\text{Ni}_8]$ unit (Fig. 2a). Each fragment is connected through Ni3 atoms with three other fragments rotated by 180° . Six $[\text{Ni}_8]$ units are linked together by vertices in the ab plane, building up ring units of 18 tetrahedra (Fig. 2b). The resulting substructure of Ni atoms features a two-dimensional network in the ab plane (Fig. 2c). Eu1 atoms fill holes in the hexagonal rings thus formed; Eu2 and In1 atoms separate different sheets of nickel networks. The vertices of the tetrahedra in the next layer are located under the centers of the hexagonal rings. The orientation of the layers in the structure can be described as an ABC sequence (Fig. 2d). The different nickel clusters have been found for several compounds with a high content of transition element in RE–Ni–In systems (RE is a rare earth): a three-dimensional network of ${}^3_\infty[\text{Ni}_4]$ corner-sharing tetrahedra is a characteristic of CeNi_4In (Koterlin *et al.*, 1998), two-dimensional ${}^2_\infty[\text{Ni}_2]$ fragments occur in LaNi_2In (Kalychak & Zaremba, 1994) and one-dimensional ${}^1_\infty[\text{Ni}_5]$ and ${}^1_\infty[\text{Ni}_7]$ cluster chains are present in $\text{Ce}_4\text{Ni}_7\text{In}_8$ (Baranyak, Kalychak *et al.*, 1988) and EuNi_7In_6 (Zaremba *et al.*, 2006), respectively.

Previously, the hexagonal EuNi_5In (h- EuNi_5In ; Baranyak *et al.*, 1992) intermetallic of the CeNi_5Sn type was observed at 670 K. The synthesis of our compound was carried out at 870 K. Therefore, we believe that the new compound with the UCu_5In type is probably a high-temperature polymorphic modification of h- EuNi_5In with the CeNi_5Sn type. Structures of both intermetallics can be considered as an intergrowth of

**Figure 3**

The packing of (c) CaCu_5 -, (d) MgCu_2 - and (e) NiAs -related slabs in the (a) UCu_5In and (b) CeNi_5Sn forms of EuNi_5In .

the CaCu_5 (Bruzzone, 1971), MgCu_2 (Ohba *et al.*, 1984) and NiAs (Brand & Briest, 1965) related slabs (Fig. 3) with the compositions EuNi_5 , InNi_2 and EuNi in the ratio of 1:2:1, *viz.* $2\text{EuNi}_5\text{In} = \text{EuNi}_5 + 2\text{InNi}_2 + \text{EuNi}$. Hence, the unit cell of each compound in the orthorhombic projection is deduced as follows: for the UCu_5In structure type, $3\text{Eu}_2\text{Ni}_{10}$ (6CaCu_5) + $6\text{In}_2\text{Ni}_4$ (12MgCu_2) + $3\text{Eu}_2\text{Ni}_2$ (6NiAs) = $\text{Eu}_{12}\text{Ni}_{60}\text{In}_{12} = 12$ r- EuNi_5In ; and for the CeNi_5Sn structure type, $2\text{Eu}_2\text{Ni}_{10}$ (4CaCu_5) + $4\text{In}_2\text{Ni}_4$ (8MgCu_2) + $2\text{Eu}_2\text{Ni}_2$ (4NiAs) = $\text{Eu}_8\text{Ni}_{40}\text{In}_8 = 8$ h- EuNi_5In . In both structures, the fragments alternate along the c axis. Consequently, the unit-cell dimension c is proportional to the number of layers: the hexagonal phase has two sets of fragments and $c \simeq 20 \text{ \AA}$, and the rhombohedral phase has three sets of fragments and $c \simeq 30 \text{ \AA}$. It should be noted that the original prototype UCu_5In of the novel compound (Stępień-Damm *et al.*, 1999; Hlukhyy, 2003) has three polymorphic modifications, two of which have the same structure as reported herein.

Experimental

A sample of composition EuNi_4In and a weight of 2 g was prepared by arc-melting of the pure components (the purity of the ingredients was higher than 99.9 wt%) under a high-purity argon atmosphere. The ingot was remelted twice to ensure homogeneity. The sample was wrapped in tantalum foil and sealed in an evacuated quartz tube. The ampoule was heated to 1070 K, followed by cooling to 870 K for 24 h. The annealing was carried out at this temperature for 75 h. After the thermal treatment, the ampoule with samples was quenched in water. The sample obtained showed a small weight loss which could be explained by evaporation of Eu. The sample is air and moisture sensitive and decomposes outside of the inert atmosphere within a few days. An X-ray diffraction powder pattern was collected using monochromatic $\text{Cu K}\alpha$ radiation on a DRON-3 diffractometer. X-ray phase analysis revealed the presence of two phases, *viz.* EuNi_5In and a small amount of In, which could be explained by a partial decomposition of the sample. Single crystals of EuNi_5In of an irregular form were extracted from the crushed sample. In contrast to the powder, these remain stable in air for a long time.

Crystal data

EuNi_5In	$Z = 6$
$M_r = 560.33$	Mo $K\alpha$ radiation
Trigonal, $R\bar{3}m$	$\mu = 42.64 \text{ mm}^{-1}$
$a = 4.8956$ (7) \AA	$T = 293 \text{ K}$
$c = 29.751$ (6) \AA	$0.15 \times 0.10 \times 0.05 \text{ mm}$
$V = 617.51$ (18) \AA^3	

Data collection

Bruker CCD diffractometer	1820 measured reflections
Absorption correction: empirical (using intensity measurements) (Blessing, 1995)	229 independent reflections
$T_{\min} = 0.003$, $T_{\max} = 0.100$	209 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$	20 parameters
$wR(F^2) = 0.051$	$\Delta\rho_{\text{max}} = 2.55 \text{ e \AA}^{-3}$
$S = 1.08$	$\Delta\rho_{\text{min}} = -1.31 \text{ e \AA}^{-3}$
229 reflections	

Analyses of the systematic absences for the single-crystal data led to the possible space groups $R\bar{3}$ (No. 148), $R3$ (No. 146), $R3m$ (No. 160), $R32$ (No. 155) and $R\bar{3}m$ (No. 166). The space group with the highest symmetry, $R\bar{3}m$, was found to be correct during the structure refinement. The starting atomic parameters were deduced from an automatic interpretation of direct methods and the structure was successfully refined with anisotropic atomic displacement parameters for all atoms. All crystallographic positions are fully occupied. Final difference Fourier synthesis revealed a slightly elevated, but not significant, residual peak of 2.55 e \AA^{-3} . However, it was too close to an Ni-atom position (0.90 \AA) to be indicative of an additional atomic site. It is probably due to the irregular shape of the crystal and consequently an incomplete absorption correction.

Data collection: *SMART* (Bruker, 1996); cell refinement: *SAINTE* (Bruker, 1996); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KU3048). Services for accessing these data are described at the back of the journal.

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