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The Indide $Er_{2.30(1)}Ni_{1.84(1)}In_{0.70(1)}$ – A New Superstructure of the U_3Si_2 Family

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Summary. Single crystals of the indide $Er_{2.30(1)}Ni_{1.84(1)}In_{0.70(1)}$ were isolated from an arc-melted sample of the initial composition 5Er:2Ni:1In. $Er_{2.30}Ni_{1.84}In_{0.70}$ crystallizes with a new superstructure of the Mo_2FeB_2 type: $P4/m$, $a = 738.6(2)$, $c = 361.4(1)$ pm, $wR2 = 0.0393$, 487 F^2 values, 22 variables, $BASF = 0.500(3)$ (meroedric twin matrix 010 100 00$\bar{1}$). The structure may be described as an intergrowth variant of slightly distorted AlB_2 and CsCl related slabs. Formation of the superstructure results in two crystallographically independent sites 1*a* and 1*c* that center the CsCl slab. These sites have different size and they are occupied by 90% In + 10% Er (1*c*) and 51% In + 49% Er (1*a*), respectively. The crystal chemical consequences are discussed on the basis of a group-subgroup scheme.

Keywords. Rare earth compounds; Crystal chemistry; Superstructure.

Introduction

The Mo_2FeB_2 type structure [1] space group $P4/mbm$, a ternary ordered variant of U_3Si_2 [2, 3], can be considered as a simple 1:1 intergrowth variant of slightly distorted AlB_2 and CsCl related slabs. So far, more than 100 intermetallic R_2T_2X and $R_2X'_2X$ (R = rare earth or actinoid metal, T = late transition metal, X = element of the 3rd, 4th, or 5th main group) compounds have been reported [4–6]. Their crystal chemistry and physical properties are summarized in a recent review article [4]. While most R_2T_2X intermetallics have been reported with the ideal composition, there are some others that show tendencies for defects or solid solutions, *i.e.* $R_2T_{2-x}X$, $R_2T_{2+x}X_{1-x}$ or $R_{2+x}T_2X_{1-x}$.

Furthermore, due to a puckering effect, some R_2T_2X compounds show the formation of a superstructure upon doubling the subcell c parameter, resulting in

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a *klassengleiche* symmetry reduction of index 2 (k2) from space group $P4/mbm$ to space group $P4_2/mnm$. This kind of superstructure has first been observed for U_2Pt_2Sn [7] and Er_2Au_2Sn [8].

During our recent phase analytical investigations of the Tm–Ni–In system [9, 10], we synthesized the two indides $Tm_2Ni_{1.896}In$ and $Tm_{2.22}Ni_{1.81}In_{0.78}$ which show nickel defects and Tm/In mixing. Both compounds, however, still crystallize in space group $P4/mbm$, and there was no indication for a symmetry reduction. With the slightly larger erbium atoms we have obtained an indide of nearly similar composition $Er_{2.30}Ni_{1.84}In_{0.70}$. The latter, however, showed formation of a new superstructure variant. The structure refinement and crystal chemistry of $Er_{2.30}Ni_{1.84}In_{0.70}$ are reported herein.

Discussion

New indide $Er_{2.30}Ni_{1.84}In_{0.70}$ adopts an intergrowth structure of distorted AlB_2 and CsCl related slabs within the family of U_3Si_2 related intermetallics. Since the crystal chemistry of such materials has been described in detail in a recent review article [4], we focus here on the comparison with the undistorted structures of $Er_2Ni_{2-x}In$ [17] and $Tm_{2.22}Ni_{1.81}In_{0.78}$ [10]. Since $Er_{2.30}Ni_{1.84}In_{0.70}$ described herein has a larger erbium content within the distorted CsCl slabs, the *a* lattice parameter of 738.6 pm is larger than that for $Er_2Ni_{2-x}In$ (731.0 pm) [17]. In contrast, the *c* parameter slightly contracts from 365.4 ($Er_2Ni_{2-x}In$) to 361.4 pm, and there is a slight increase of the cell volume for the erbium richer phase.

The nickel site in $Er_{2.30}Ni_{1.84}In_{0.70}$ is not fully occupied. This has also been observed for the whole series of $RE_2Ni_{2-x}In$ [17] and $RE_2Ni_{2-x}Cd$ [18] intermetallics and $Tm_{2.22}Ni_{1.81}In_{0.78}$ [10]. The nature of these nickel deficits is still not well understood. In view of the Er/In mixing and the nickel deficits in $Er_{2.30}Ni_{1.84}In_{0.70}$, one can write a general formula $Er_{2+x}Ni_{2-y}In_{1-x}$, emphasizing the homogeneity range.

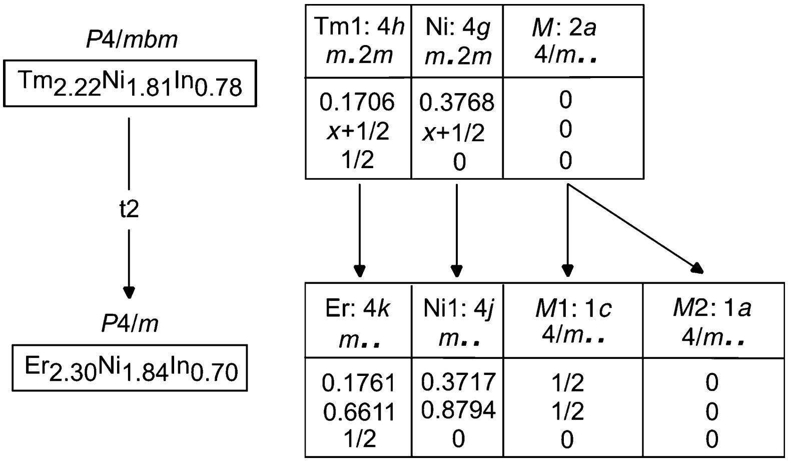

Fig. 1. Group-subgroup scheme in the *Bärnighausen* formalism [14, 15] for the structures of $Tm_{2.22}Ni_{1.81}In_{0.78}$ [10] and $Er_{2.30}Ni_{1.84}In_{0.70}$; the evolution of the atomic parameters is shown at the right-hand part; M denotes In/Tm and In/Er mixing (see Table 2 and Ref. [10])

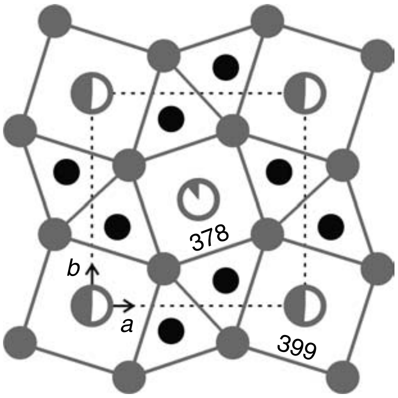

Fig. 2. Projection of the $Er_{2.30(1)}Ni_{1.84(1)}In_{0.70(1)}$ structure onto the *xy* planes; all atoms lie on mirror planes at $z = 0$ (Ni, *M*1, and *M*2) and $z = 1/2$ (Er), respectively; the erbium, nickel, and indium atoms are drawn as gray, filled, and open circles, respectively; the sectors of the indium sites correspond to the different erbium content; the AlB_2 and CsCl related slabs are emphasized

The group-subgroup scheme (Fig. 1) presented in the *Bärnighausen* formalism [14, 15] shows a decoupling of the Er and the Ni position from $x, x + 1/2$ to x, y with an independent y parameter. This way we get a distortion of both the AlB_2 and the CsCl slabs (see Fig. 2). The distortion results in larger (1*a* site) and smaller (1*c* site) CsCl slabs. The Er–Er distances of the square faces in the *ab* plane are 399 and 378 pm, respectively. The shortest Er–Er distances are located within the AlB_2 slab, *i.e.* 353 pm. The shorter Er–Er contacts are similar to the average Er–Er distance of 351 in *hcp* erbium [19].

The distortions of the erbium cubes have a significant influence on the Ni–Ni distance. The latter has a value of 260 pm, somewhat longer than in $Tm_{2.22}Ni_{1.81}In_{0.78}$ (256 pm), $Tm_2Ni_{1.896}In$ (250 pm), and elemental nickel (249 pm) [19]. We can thus assume weaker Ni–Ni bonding in $Er_{2.30}Ni_{1.84}In_{0.70}$. The same holds true for the Ni–*M* distances of 289 and 296 pm (Table 1). They are much longer than the sum of the covalent radii of 259 pm [20] for Ni + In.

The Er–Ni distances range from 282 to 285 pm, close to the sum of the covalent radii of 272 pm [20]. Similar to the structure of Sc_2Ni_2In [21], these Er–Ni contacts

Table 1. Interatomic distances (pm) in $Er_{2.30(1)}Ni_{1.84(1)}In_{0.70(1)}$, calculated with the powder lattice parameters; standard deviations are all equal or less than 0.2 pm; all distances within the first coordination spheres are listed; for the mixed In/Er occupancies of *M*1 and *M*2 see Table 2

Er:	2	Ni	281.9	Ni:	1	Ni	260.2
	2	Ni	282.9		2	Er	281.9
	2	Ni	285.1		2	Er	282.9
	2	*M*1	322.6		2	Er	285.1
	2	*M*2	335.0		1	*M*2	288.6
	1	Er	352.6		1	*M*1	295.8
	2	Er	361.4	*M*1:	4	Ni	295.8
	2	Er	377.9		8	Er	322.6
	2	Er	398.9	*M*2:	4	Ni	288.6
					8	Er	335.0

Table 2. Atomic coordinates and anisotropic displacement parameters (pm^2) of $Er_{2.30(1)}Ni_{1.84(1)}In_{0.70(1)}$; U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor; the anisotropic displacement factor exponent takes the form $-2\pi^2[(ha^*)^2U_{11} + \ldots + 2kha^*b^*U_{12}]$; $U_{13} = U_{23} = 0$

Atom	*Wyck.*	Occupancy/%	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{eq}
Er	4*k*	100	0.17611(5)	0.66112(6)	1/2	143(2)	179(2)	104(1)	−40(1)	142(1)
Ni	4*j*	92.0(5)	0.3717(2)	0.8794(2)	0	142(6)	116(5)	143(4)	−19(3)	134(3)
*M*1	1*c*	90(2) In + 10(2) Er	1/2	1/2	0	114(4)	U_{11}	172(6)	0	133(4)
*M*2	1*a*	51(2) In + 49(2) Er	0	0	0	119(4)	U_{11}	153(5)	0	130(3)

can be considered as strongly bonding. The next nearest neighbours Er–*M* have significantly longer distances from 323–335 pm. This is certainly related to the erbium/indium mixing.

Finally we need to compare the structure of $Er_{2.30}Ni_{1.84}In_{0.70}$ with that of Zr_5Ni_4Al [22]. In contrast to $Er_{2.30}Ni_{1.84}In_{0.70}$, the aluminide shows a complete ordering of the zirconium and aluminum atoms and a clear doubling of the subcell *c* axis, leading to the *klassengleiche* subgroup $P4_2/m$. Since both one-fold sites in the $Er_{2.30}Ni_{1.84}In_{0.70}$ structure show a different Er/In mixing (Table 2), an ordering is not possible. Thus we only observe two different sizes of the CsCl related slabs. This is realized through the symmetry reduction to space group $P4/m$. The loss of the high *Laue* symmetry causes twinning by merohedry (by chance 50/50 for the investigated crystal). This situation is similar for the recently reported $Gd_3Rh_{1.940(7)}In_4$ structure [23]. Here, the ordering of rhodium and indium lowers the space group symmetry from $P\bar{6}2m$ to $P\bar{6}$ and also that crystal showed twinning by merohedry.

Another difference between the structures of $Er_{2.30}Ni_{1.84}In_{0.70}$ and Zr_5Ni_4Al is the behaviour of the nickel atoms. If a superstructure forms, like the Zr_3Al_2 [4] or the Zr_5Ni_4Al type, the Ni_2 pairs dislocate from the subcell mirror planes. In those cases, the U_{33} values are extremely large, if only the subcell structures are refined. For $Er_{2.30}Ni_{1.84}In_{0.70}$ reported herein, the nickel atoms give no hint for such a displacement!

Experimental

Synthesis

Starting materials for the synthesis of the erbium nickel indides were ingots of erbium (Johnson Matthey), nickel wire (Johnson Matthey, Ø 0.38 mm), and indium tear drops (Heraeus), all with stated purities better than 99.9%. The larger erbium ingot was mechanically cut into smaller pieces and the latter were arc-melted [11] to small buttons under an argon atmosphere of *ca.* 600 mbar. The argon was purified before over titanium sponge (900 K), silica gel, and molecular sieves. The premelting of the rare earth element strongly reduces shattering during the exothermic reaction with nickel and indium. $Er_{2.30}Ni_{1.84}In_{0.70}$ was first obtained as a side product during an attempt to grow single crystals of the indide Er_5Ni_2In with Mo_5B_2Si structure [10]. Later we obtained this indide from a sample with the starting composition Er:Ni:In = 2.30:1.84:0.70. The elements were placed in a water-cooled copper crucible of an arc-melting furnace and first reacted under an argon pressure of *ca.* 600 mbar. The product button was remelted three times in order to ensure homogeneity. $Er_{2.30}Ni_{1.84}In_{0.70}$ was obtained in an amount of 500 mg. This indide is air-stable as a compact button as well as a fine-grained powder. Polycrystalline $Er_{2.30}Ni_{1.84}In_{0.70}$ is brittle and light gray. Single crystals exhibit metallic lustre, while coarsly grained powders are dark gray.

Scanning Electron Microscopy

The single crystal investigated on the image plate diffractometer was analyzed in a LEICA 420I scanning electron microscope using ErF_3, Ni, and InAs as standards. The EDX analyses showed a composition of 47 ± 3 at-% Er: 34 ± 3 at-% Ni: 19 ± 3 at-% In, close to the composition of 47:38:15 obtained from the single crystal X-ray data (see below). The relatively large uncertainties for the EDX data account for the various analyses made on different points of the irregularly shaped crystal.

X-Ray Film Data and Structure Refinement

The samples were characterized *via Guinier* powder patterns using Cu $K\alpha_1$ radiation and α-quartz ($a = 491.30$, $c = 540.46$ pm) as an internal standard. The *Guinier* camera was equipped with an image plate system (Fujifilm, BAS-1800). The tetragonal lattice parameters (Table 3) were obtained from least-squares fits to the *Guinier* data. The correct indexing of the diffraction lines was ensured through an intensity calculation [12] using the atomic positions obtained from the structure refinement. The X-ray powder and single crystal ($a = 739.4(1)$, $c = 361.24(7)$ pm) lattice parameters agreed well.

Table 3. Crystal data and structure refinement for $Er_{2.30(1)}Ni_{1.84(1)}In_{0.70(1)}$, space group $P4/m$; $Z = 2$

Empirical formula	$Er_{2.30(1)}Ni_{1.84(1)}In_{0.70(1)}$
Molar mass	572.51 g/mol
Unit cell dimensions (*Guinier* powder)	$a = 738.6(2)$ pm
	$c = 361.4(1)$ pm
	$V = 0.1972\,nm^3$
Calculated density	$9.64\,g/cm^3$
Crystal size	$30 \times 60 \times 70\,\mu m^3$
Detector distance	60 mm
Exposure time	8 min
ω range; increment	0–180°; 1.0°
Integr. param. A, B, EMS	13.5; 3.5; 0.012
Transm. Ratio (max/min)	4.15
Absorption coefficient	$60.8\,mm^{-1}$
$F(000)$	484
θ range	3° to 35°
Range in hkl	±11, ±11, ±5
Total no. reflections	2904
Independent reflections	487 ($R_{int} = 0.0412$)
Reflections with $I > 2\sigma(I)$	479 ($R_\sigma = 0.0221$)
Data/parameters	487/22
Goodness-of-fit on F^2	1.175
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0211$
	$wR2 = 0.0392$
R indices (all data)	$R1 = 0.0217$
	$wR2 = 0.0393$
Twin matrix	010 100 00$\bar{1}$
BASF	0.500(3)
Extinction coefficient	0.043(2)
Largest difference peak and hole	$1.61/-1.66\,e/\AA^3$

Irregularly-shaped silvery single crystals were isolated from the crushed sample, mounted on glass fibres using bees wax, and first examined on a *Buerger* precession camera in order to check the quality for intensity data collection. Also the *Buerger* camera was equipped with the same image plate system.

Structure Refinement

Intensity data were collected at room temperature on a *Stoe* IPDS-II image plate diffractometer using graphite monochromatized Mo K_α radiation (71.073 pm). A numerical absorption correction was applied to the data set (XSHAPE, refinement/optimisation of the crystal shape and size). All relevant crystallographic data and details about the data collection are listed in Table 3.

In the first stage of the refinement we have assumed isotypism with the thulium compound $Tm_{2.22}Ni_{1.81}In_{0.78}$, space group $P4/mbm$, since the EDX analyses showed a comparable composition. A refinement of the structure assuming the positional parameters of $Tm_{2.22}Ni_{1.81}In_{0.78}$ [10], however, did not converge to low residuals. Furthermore, the erbium position showed an enhanced U_{11} and U_{22} parameter and a relatively large standard deviation for the x parameter. This was already indicative for a symmetry problem. Careful re-examination of the data set indeed revealed *Laue* symmetry $4/mmm$. Thus, low *Laue* symmetry $4/m$ in combination with merohedric twinning (50/50) would be a possible explanation for the symmetry problem.

We have then checked the possible subgroups [13] and finally $P4/m$ turned out to be the correct space group. As indicated in the *Bärnighausen* tree [14, 15] in Fig. 1, in space group $P4/m$ the erbium and nickel atoms gain a free y parameter, and an ordering of the $2a$ supergroup site *via* two one-fold sites is possible. We have transformed the positional parameters to the setting of space group $P4/m$ and the structure was refined with anisotropic displacement parameters for all atoms using SHELXL-97 (full-matrix least-squares on F_o^2) [16]. This refinement clearly showed two different mixed Er/In occupancies on the sites $1a$ and $1c$, but the final residuals were still not satisfying ($R1 = 0.0984$; $wR2 = 0.2064$). Finally it turned out that the crystal showed twinning by merohedry, caused by the *translationengleiche* symmetry reduction as could be expected by the group-subgroup relation. Subsequently the twin matrix ($010\ 100\ 00\bar{1}$) was introduced. Now the structure refinement converged smoothly to the residuals listed in Table 3 with a twin ratio of 50/50. The latter might be a hint for an ordering of the atoms and an enlargement of the unit cell. Careful examination of the image plate data, however, revealed no superstructure reflections. The nickel site revealed a small deficit, as is frequently observed in U_3Si_2 related intermetallics [4]. A final difference *Fourier* synthesis did not reveal significant residual peaks. The refined atomic positions and a list of the interatomic distances are given in Tables 1 and 2. Further details on the structure refinement may be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No. CSD-415309.

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