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# CRYSTAL STRUCTURE OF THE $Sc_{1-x}Co_2In_x$ ($x$=0–0.26) SOLID SOLUTION

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Formation of the $Sc_{1-x}Co_2In_x$ ($x$ = 0–0.26) solid solution ($MgCu_2$ type structure, space group *Fd*-3*m*) has been established during the investigation of the phase equilibria in the Sc–Co–In system at 870 K. The crystal structure has been investigated for the $Sc_{0.96}Co_2In_{0.04}$ ($a$ = 6.91154(10) Å, $Z$ = 8, $R_1$ = 0.0167, $wR_2$ = 0.0441) and $Sc_{0.78}Co_2In_{0.22}$ ($a$ = 6.93072(14) Å, $Z$ = 8, $R_1$ = 0.0201, $wR_2$ = 0.0465) compositions using X-ray single crystal diffraction data. Unit cell parameters increase with increasing of indium content in the solid solution according to atomic radii of the elements.

*Keywords*: scandium, cobalt, indium, intermetallic, crystal chemistry.

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Phase interactions in ternary systems of rare earth metals (R) with transition elements, especially Ni, Co, Cu, and indium have been investigated intensively because of existence of numerous compounds with different crystal structures and interesting physical properties. Up to now, more than 70 compounds were reported to occur in the R–Co–In systems [1]. However, isothermal sections of the phase diagrams have been built only for Ce–Co–In [2] and Er–Co–In [3] systems.

Sc–Co–In system has not been investigated systematically as yet. One ternary compound $Sc_6Co_{2.18}In_{0.82}$ (space group *Immm*, $a$ = 8.867, $b$ = 8.780, $c$ = 9.321 Å) was reported in 2006 [4]. Afterwards we determined crystal structure of $Sc_5Co_2In_4$ (space group *Pbam*, $a$ = 17.3400, $b$ = 7.5940, $c$ = 3.3128 Å) using a single crystal X–ray diffraction method [5]. Crystal structures of four other compounds we resolved using the results of X–ray powder diffraction: $Sc_3Co_{1.69}In_4$ (space group *P*-6, $a$ = 7.6598, $c$ = 3.3617 Å), $Sc_{10}Co_9In_{19.60}$ (space group *P*4/*nmm*, $a$ = 12.8220, $c$ = 9.0338 Å) [6], $Sc_2CoIn$ (space group *P*4/*mmm*, $a$ = 3.2887, $c$ = 7.1642 Å) and $Sc_{100}Co_{25}In_7$ (space group *Fm*-3, $a$ = 17.7411 Å) [7].

According to phase diagram of the Sc-Co binary system reported in Ref. [8], $ScCo_2$ adopts $MgCu_2$ type structure and at 870 K exists in $Sc_{31}Co_{69}$–$Sc_{36}Co_{64}$ region. At 1073 K unit cell parameter $a$ increases linearly from 6.892 (for $Sc_{30}Co_{70}$) to 6.921 Å (for $Sc_{34.5}Co_{65.5}$) [9].

Scandium and indium atoms have similar radii, which makes possible formation of substitutional solid solutions in the Sc–Co–In ternary system. Investigation of the $Sc_{1-x}Co_2In_x$ ($x$ = 0–0.26) solid solution in the Sc–Co–In system at 870 K is the purpose of the present paper.

High purity metals (scandium – 99.9; cobalt – 99.92; indium – 99.99 wt. %) were used for synthesis of alloys. Despite a variable composition of $ScCo_2$ compound (64–69 at. % of Co [8]) we decided to choose for investigation samples with 66.7 at. % Co. Three samples $Sc_{28}Co_{66.7}In_{5.3}$, $Sc_{22}Co_{66.7}In_{11.3}$ and $Sc_{16.7}Co_{66.7}In_{16.6}$ with an average mass ≈1.0 g. were arc–melted in atmosphere of high purity argon. Losses after melting were less than 1 wt. %. The melted samples were sealed in evacuated silica tubes and annealed at 870 K during two months. After annealing the tubes with the alloys were quenched in cold water.

Two single crystals were selected from $Sc_{28}Co_{66.7}In_{5.3}$ and $Sc_{22}Co_{66.7}In_{11.3}$ samples. Their X–ray diffraction data were collected using an Oxford Diffraction Xcalibur four–circle single–crystal X–ray diffractometer with CCD Atlas detector (graphite–monochromatized $MoK_\alpha$ radiation, λ = 0.71073 Å). Raw data were treated with a CrysAlis Data Reduction program taking into account an absorption correction. Intensities of the reflections were corrected for Lorentz and polarization factors. The crystal structure was solved by Patterson methods and refined by full-matrix least–squares method using SHELXL–2014 [10]. X-ray powder diffraction data were collected with Stoe IPDS diffractometer ($CuK_\alpha$ radiation). EDX analysis of $Sc_{16.5}Co_{67}In_{16.5}$ sample has been performed using scanning electron microscope REMMA–102–02.

The $Sc_{16.7}Co_{66.7}In_{16.6}$ sample consisted of three phases according to the data of EDX analysis: $Sc_{18}Co_{65}In_{17}$ (main grey phase – $ScCo_4In$), $Sc_{23}Co_{68}In_9$ (dark phase – solid solution on the base of $ScCo_2$) and $Sc_{25}Co_{30}In_{44}$ (light phase – unknown compound) (Fig. 1). According to these results phase $Sc_{23}Co_{68}In_9 \equiv Sc_{0.74}Co_2In_{0.26}$ can be considered as the border of the solid solution. Different values of unit cell parameter for cubic phase with the structure of $MgCu_2$ – type in the investigated alloys proved formation of the solid solution on the base of $ScCo_2$.

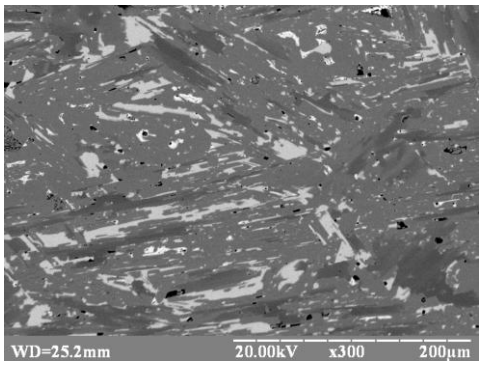


Fig. 1. Electron micrograph of $Sc_{16.7}Co_{66.7}In_{16.6}$ sample (see text)

Therefore, formation of the $Sc_{1-x}Co_2In_x$ ($x$ = 0–0.26) solid solution along concentration 66.7 at. % Co ($MgCu_2$ – type structure, space group *Fd*-3*m*) has been established in Sc–Co–In system at 870 K.

The crystal structure of this solid solution was determined using X–ray single crystal diffraction data. Table 1 presents summarized crystal data and refinement information, whereas the atomic coordinates and the displacement parameters are listed in Table 2. The interatomic distances and the coordination numbers (CN) of the atoms are presented in Table 3. All the main interatomic distances are close to the sums of the respective atomic radii of Sc (1.606 Å), Co (1.253 Å) and In (1.626 Å) [11].

*Table 1*

Crystal data and structure refinement details for $Sc_{0.96}Co_2In_{0.04}$ and $Sc_{0.78}Co_2In_{0.22}$

| | | |
|---|---|---|
| Nominal composition | $Sc_{28}Co_{66.7}In_{5.3}$ | $Sc_{22}Co_{66.7}In_{11.3}$ |
| Refined composition | $Sc_{0.96}Co_2In_{0.04}$ | $Sc_{0.78}Co_2In_{0.22}$ |
| Formula weight, g/mol | 165.35 | 178.19 |
| Space group | *Fd*-3*m* (No. 227) | *Fd*-3*m* (No. 227) |
| Unit cell parameter, Å | $a$ = 6.91154(10) | $a$ = 6.93072(14) |
| Volume, Å$^3$ | 330.160(14) | 332.92(2) |
| Number of formula units per unit cell | 8 | 8 |
| Calculated density, g/cm$^3$ | 6.65 | 7.11 |
| Absorption coefficient, cm$^{-1}$ | 23.57 | 25.17 |
| $F$(000) | 608 | 649 |
| Crystal color | silver | silver |
| Crystal size, mm | 0.058×0.039×0.033 | 0.077×0.029×0.024 |
| Diffractometer | Oxford Diffraction Xcalibur | |
| $\theta$ range for data collection | 5.109 – 32.299 | 5.095 – 32.198 |
| *hkl* indexes ranges | –10≤$h$≤10 | –9≤$h$≤9 |
| | –10≤$k$≤10 | –10≤$k$≤10 |
| | –9≤$l$≤10 | –9≤$l$≤9 |
| Reflections collected | 1954 | 1404 |
| Independent reflections | 45 | 42 |
| | [R(int.)=0.0221] | [R(int.)=0.0274] |
| Refinement method | Full-matrix least-square on $F^2$ | |
| Data/restraints/parameters | 45/0/5 | 42/0/5 |
| Goodness-of-fit on $F^2$ | 1.51 | 1.38 |
| Final $R$ indices [$I>2\sigma(I)$] | $R_1$=0.0167, $wR_2$=0.0441 | $R_1$=0.0201, $wR_2$=0.0465 |
| $R$ indices (all data) | $R_1$=0.0167, $wR_2$=0.0441 | $R_1$=0.0201, $wR_2$=0.0465 |
| Largest diff. peak and hole, e/Å$^3$ | 0.46 and –0.63 | 1.44 and –1.04 |

*Table 2*

Atomic coordinates and thermal displacement parameters (×10$^4$ Å$^2$) for $Sc_{0.96}Co_2In_{0.04}$ and $Sc_{0.78}Co_2In_{0.22}$

| Atom | Position | *x/a* | *y/b* | *z/c* | $U_{eq.}$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $Sc_{0.96}Co_2In_{0.04}$ | | | | | | | | | | | |
| M* | 8*b* | 3/8 | 3/8 | 3/8 | 96(5) | 96(5) | 96(5) | 96(5) | 0 | 0 | 0 |
| Co | 16*c* | 0 | 0 | 0 | 60(3) | 60(3) | 60(3) | 60(3) | –8.1(13) | –8.1(13) | –8.1(13) |
| $Sc_{0.78}Co_2In_{0.22}$ | | | | | | | | | | | |
| M** | 8*b* | 3/8 | 3/8 | 3/8 | 84(6) | 84(6) | 84(6) | 84(6) | 0 | 0 | 0 |
| Co | 16*c* | 0 | 0 | 0 | 66(4) | 66(4) | 66(4) | 66(4) | –2(3) | –2(3) | –2(3) |

M* = 0.963(7) Sc + 0.037(7) In.
M** = 0.780(11) Sc + 0.220(11) In.
$U_{eq.}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.
The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

*Table 3*

Interatomic distances ($\delta$, Å) and coordination numbers (CN) of the atoms in crystal structure of the $Sc_{0.96}Co_2In_{0.04}$ and $Sc_{0.78}Co_2In_{0.22}$

| Atoms | | $\delta$, Å | | CN |
|---|---|---|---|---|
| | | $Sc_{0.96}Co_2In_{0.04}$ | $Sc_{0.78}Co_2In_{0.22}$ | |
| M | –12Co | 2.86537(3) | 2.87332(6) | 16 |
| | –4M | 2.99278(3) | 3.00109(4) | |
| Co | –6Co | 2.44360(3) | 2.45038(5) | 12 |
| | –6M | 2.86537(4) | 2.87332(6) | |

Fig. 2 displays projection of the unit cell of $Sc_{1-x}Co_2In_x$ ($x$ = 0–0.26) solid solution on the *XY* plane and coordination polyhedra of M (Sc/In) and Co atoms. Cobalt atoms occupy solely one crystallographic position, while Sc and In atoms share another position. Co atoms are inside icosahedra [$CoM_6Co_6$], and M atoms are in 16–vertex Frank–Kasper polyhedra [$MM_4Co_{12}$].

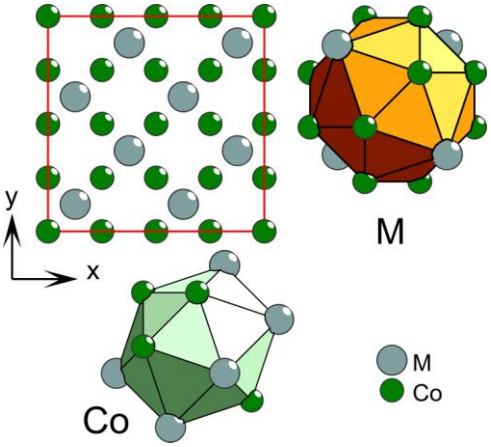


Fig. 2. Projection of the unit cell of $Sc_{1-x}Co_2In_x$ ($x$=0–0.26) on the *XY* plane and the coordination polyhedra of M (Sc/In) and Co atoms

Compositions of $Sc_{0.96}Co_2In_{0.04}$ and $Sc_{0.78}Co_2In_{0.22}$ single crystals were determined from single crystal diffraction data and have lower indium content in comparison with nominal compositions of alloys they were extracted from. Latter composition, obviously, can be considered as one close to the border of the solid solution $Sc_{1-x}Co_2In_x$ ($x$ = 0–0.26, by EDX analysis) at 870 K.

X–ray single crystal structure determination confirms that lattice constants increase with increasing In content in alloys: for composition of $Sc_{0.96}Co_2In_{0.04}$ $a$ = 6.91154(10) Å, while for $Sc_{0.78}Co_2In_{0.22}$ parameter $a$ is equal to 6.93072(14) Å. The change of the unit cell parameter $a$ for the solid solution $Sc_{1-x}Co_2In_x$ ($x$ = 0–0.26) is shown in Fig.3. The lattice parameter $a$ for binary $ScCo_2$ is taken from the Ref. [9, 12–14]. The increasing of unit cell parameter at substitution of Sc by In correlate well with the sizes of atomic radii [11].

Such solid solutions were also found in R–Ni–In ternary systems, where R is a heavy rare–earth element, e.g. $Er_{1-0.76}Ni_2In_{0-0.24}$ [15], $Dy_{1-0.50}Ni_2In_{0-0.50}$ [16] and $Tm_{1-0.50}Ni_2In_{0-0.50}$ [17]. In Er–Co–In system, however, solid solution ($Er_{1-0.72}Co_3In_{0-0.28}$) adopts $PuNi_3$ – type structure [3].

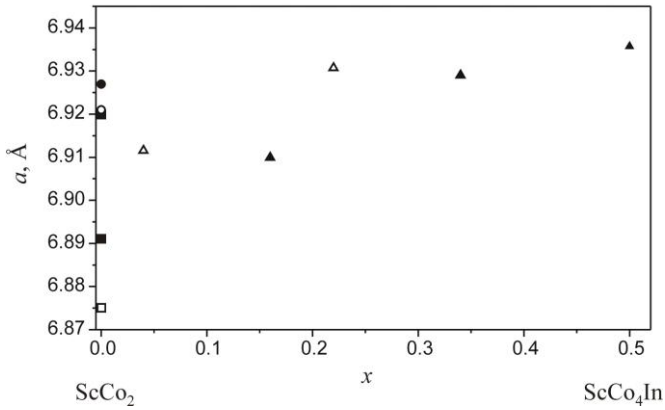


Fig. 3. Unit cell parameter *a* vs. *x* value for the $Sc_{1-x}Co_2In_x$ (*x*=0–0.26) solid solution. Empty triangles correspond to single crystal data and solid triangles – to powder data. Literature data on parameter *a* for $ScCo_2$ were taken from Ref. [9] – solid square; [12] – empty square; [13] – solid circle and [14] – empty circle

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## КРИСТАЛІЧНА СТРУКТУРА ТВЕРДОГО РОЗЧИНУ $Sc_{1-x}Co_2In_x$ (x=0–0,26)

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Діаграма стану системи Sc–Co–In систематично не досліджена. З літератури відома низка тернарних сполук системи: $Sc_6Co_{2,18}In_{0,82}$ (просторова група *Immm*, *a* = 8,867, *b* = 8,780, *c* = 9,321 Å), $Sc_5Co_2In_4$ (*Pbam*, *a* = 17,3400, *b* = 7,5940, *c* = 3,3128 Å), $Sc_3Co_{1,69}In_4$ (*P*-6, *a* = 7,6598, *c* = 3,3617 Å), $Sc_{10}Co_9In_{19.60}$ (*P*4/*nmm*, *a* = 12,8220, *c* = 9,0338 Å), $Sc_2CoIn$ (*P*4/*mmm*, *a* = 3,2887, *c* = 7,1642 Å) і $Sc_{100}Co_{25}In_7$ (*Fm*-3, a = 17,7411 Å).

Під час дослідження фазових рівноваг у системі Sc–Co–In при 870 K виявлене утворення твердого розчину $Sc_{1-x}Co_2In_x$ (*x*=0–0,26, структурний тип $MgCu_2$, просторова група *Fd*-3*m*).

Методом електродугового плавлення у атмосфері чистого аргону синтезовано три зразки при складах: $Sc_{28}Co_{66,7}In_{5,3}$, $Sc_{22}Co_{66,7}In_{11,3}$ та $Sc_{16,7}Co_{66,7}In_{16,6}$. Твердий розчин досліджували рентгенівськими дифракційними методами порошку (дифрактометр Stoe IPDS, випромінювання $CuK_\alpha$) та монокристала (чотирикружний дифрактометр Oxford Diffraction з детектором CCD Atlas, випромінювання $MoK_\alpha$), а також методом EDX аналізу (растровий електронний мікроскоп з рентгенівським мікроаналізатором РЕММА–102–02).

За даними EDX аналізу зразок $Sc_{16,7}Co_{66,7}In_{16,6}$ складається з трьох фаз: $Sc_{18}Co_{65}In_{17}$ (основна фаза – $ScCo_4In$), $Sc_{23}Co_{68}In_9$ (твердий розчин на основі $ScCo_2$) та $Sc_{25}Co_{30}In_{44}$ (невідома сполука). Фазу $Sc_{23}Co_{68}In_9 \equiv Sc_{0,74}Co_2In_{0,26}$ можна розглядати як межу твердого розчину на основі $ScCo_2$.

Кристалічна структура твердого розчину досліджена методом монокристала для складів $Sc_{0,96}Co_2In_{0,04}$ ($a$ = 6,91154(10) Å, $Z$ = 8, $R_1$ = 0,0167, $wR_2$ = 0,0441) і $Sc_{0,78}Co_2In_{0,22}$ ($a$ = 6,93072(14) Å, $Z$ = 8, $R_1$ = 0,0201, $wR_2$ = 0,0465). Параметри елементарної комірки в межах твердого розчину зростають зі збільшенням вмісту Індію, відповідно до атомних радіусів Скандію (1,606 Å) та Індію (1,626 Å).

Подібні тверді розчини були знайдені у системах R–Ni–In, де R – важкий рідкісноземельний елемент, наприклад $Er_{1-0,76}Ni_2In_{0-0,24}$, $Dy_{1-0,50}Ni_2In_{0-0,50}$ та $Tm_{1-0,50}Ni_2In_{0-0,50}$. Однак у системі Er–Co–In твердий розчин ($Er_{1-0,72}Co_3In_{0-0,28}$) існує для структури типу $PuNi_3$.

*Ключові слова:* Скандій, Кобальт, Індій, інтерметалід, кристалохімія.

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