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CRYSTAL STRUCTURE OF THE Sc$_{1-x}$Co$_x$In$_x$ (x=0–0.26) SOLID SOLUTION

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Formation of the Sc$_{1-x}$Co$_x$In$_x$ (x = 0–0.26) solid solution (MgCu$_2$ type structure, space group $Fd-3m$) 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$_{0.86}$Co$_{0.14}$In$_4$ (a = 6.91154(10) Å, Z = 8, R$_1$ = 0.0167, wR$_2$ = 0.0441) and Sc$_{0.76}$Co$_{0.24}$In$_{3.22}$ (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$_{0.2}$Co$_{1.8}$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$_3$Co$_5$In$_2$ (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$_2$Co$_{0.69}$In$_{0.31}$ (space group P-6, a = 7.6598, c = 3.3617 Å), Sc$_{10}$Co$_{19}$In$_{60}$ (space group $P4/nmm$, a = 12.8220, c = 9.0338 Å) [6], Sc$_2$CoIn (space group $P4/nmm$, a = 3.2887, c = 7.1642 Å) and Sc$_{10}$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$_3$Co$_{69}$–Sc$_{10}$Co$_{64}$ region. At 1073 K unit cell parameter $a$ increases linearly from 6.892 (for Sc$_{10}$Co$_{70}$) to 6.921 Å (for Sc$_{34.5}$Co$_{65.5}$) [9].

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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$_x$In$_x$ ($x = 0–0.26$) 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$_{66}$In$_3$, Sc$_{28}$Co$_{66}$In$_{11.3}$ and Sc$_{16}$Co$_{66}$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$_{66}$In$_3$ and Sc$_{28}$Co$_{66}$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, $\lambda = 0.71073$ 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$_{40}$In$_{16.5}$ sample has been performed using scanning electron microscope REMMA–102–02.

The Sc$_{16.5}$Co$_{40}$In$_{16.6}$ sample consisted of three phases according to the data of EDX analysis: Sc$_{19}$Co$_{90}$In$_{17}$ (main grey phase – ScCoIn), Sc$_{22}$Co$_{69}$In$_{9}$ (dark phase – solid solution on the base of ScCo$_2$) and Sc$_{25}$Co$_{68}$In$_{4}$ (light phase – unknown compound) (Fig. 1). According to these results phase Sc$_{22}$Co$_{69}$In$_{9}$ = Sc$_{0.7}$Co$_2$In$_{0.26}$ 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$_2$.

Therefore, formation of the Sc$_{1-x}$Co$_x$In$_x$ ($x = 0–0.26$) solid solution along concentration 66.7 at. % Co (MgCu$_2$ – type structure, space group Fd-3m) 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

| Nominal composition          | Sc$_2$Co$_{0.76}$In$_{0.13}$ | Sc$_2$Co$_{0.86}$In$_{0.13}$ |
|------------------------------|-----------------------------|------------------------------|
| Refined composition          | Sc$_{0.96}$Co$_3$In$_{0.04}$ | Sc$_{0.78}$Co$_3$In$_{0.22}$ |
| Formula weight, g/mol        | 165.35                      | 178.19                       |
| Space group                  | Fd-3m (No. 227)              | Fd-3m (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           |
| Diffactometer                | Oxford Diffraction Xcalibur |                              |
| θ 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                          |
| 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 > 2σ(I)]  | R$_1$=0.0167, wR$_2$=0.0441 | R$_1$=0.0201, wR$_2$=0.0465 |
|                              | R$_1$=0.0167, wR$_2$=0.0441 | R$_1$=0.0201, wR$_2$=0.0465 |
| Largest diff. peak and hole, e/A$^3$ | 0.46 and -0.63   | 1.44 and -1.04              |

Table 2

| Atom   | Position | z/a | z/b | z/c | U$_{11}$ | U$_{12}$ | U$_{22}$ | U$_{23}$ | U$_{13}$ | U$_{12}$ |
|--------|----------|-----|-----|-----|----------|----------|----------|----------|----------|----------|
| Sc$_2$Co$_{0.96}$In$_{0.04}$ | M$^*$  | 8 b | 3/8 | 3/8 | 96(5)    | 96(5)    | 96(5)    | 96(5)    | 0        | 0        |
|       | Co       | 16 c| 0   | 0   | 0        | 60(3)    | 60(3)    | 60(3)    | -8.1(13) | -8.1(13) |
| Sc$_2$Co$_{0.78}$In$_{0.22}$ | M$^{**}$| 8 b | 3/8 | 3/8 | 84(6)    | 84(6)    | 84(6)    | 84(6)    | 0        | 0        |
|       | Co       | 16 c| 0   | 0   | 0        | 66(4)    | 66(4)    | 66(4)    | -2(3)    | -2(3)    |

M$^*$ = 0.963(7) Sc + 0.037(7) In.
M$^{**}$ = 0.780(11) Sc + 0.220(11) In.

U$_{ij}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.
The anisotropic displacement factor exponent takes the form: $-2\pi^2 [U_{11}a^2 + ... + 2hka*b*U_{12}]$.
Table 3

| Atoms | $d$, Å | $d_{Sc_{0.96}Co_{2}In_{0.04}}$ | $d_{Sc_{0.78}Co_{2}In_{0.22}}$ | CN |
|-------|--------|-----------------------------|-----------------------------|----|
| 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$_2$In$_x$ ($x=0–0.26$) 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$_6$Co$_6$], and M atoms are in 16–vertex Frank–Kasper polyhedra [MM$_4$Co$_{12}$].

Compositions of Sc$_{0.96}$Co$_2$In$_{0.04}$ and Sc$_{0.78}$Co$_2$In$_{0.22}$ 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$_2$In$_x$ ($x=0–0.26$, 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$_2$In$_{0.04}$ $a=6.91154(10)$ Å, while for Sc$_{0.78}$Co$_2$In$_{0.22}$ 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$_2$In$_x$ ($x=0–0.26$) 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$_{1-0.72}$Ni$_{0.28}$In$_{0.04}$ [15], Dy$_{1-0.50}$Ni$_{0.50}$In$_{0.05}$ [16] and Tm$_{1-0.50}$Ni$_{0.50}$In$_{0.05}$ [17]. In Er–Co–In system, however, solid solution (Er$_{1-0.72}$Co$_2$In$_{0.05}$) adopts PuNi$_3$–type structure [3].
Fig. 3. Unit cell parameter $a$ vs. $x$ value for the Sc$_{1-x}$Co$_x$In$_x$ ($x=0$–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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КРИСТАЛЛІЧНА СТРУКТУРА ТВЕРДОГО РОЗЧИНУ Sc1₁Co₂In₃, (x=0–0,26)

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Діаграма стану системи Sc–Co–In систематично не досліджена. З літератури відома низка тернірних сполук системи: Sc₃Co₁In₈2 (просторова група Immm, a = 8,867, b = 8,780, c = 9,321 Å), Sc₃Co₁In₄ (Pbam, a = 17,3400, b = 7,5940, c = 3,3128 Å), Sc₃Co₁₆In₄ (P-6, a = 7,6598, c = 3,3617 Å), Sc₁₆Co₃In₁₇ (P4/nmm, a = 12,8220, c = 9,0338 Å), Sc₂Co₅In (P4/nmm, a = 3,2887, c = 7,1642 Å) і Sc₁₆Co₂In₃ (Pm-3, a = 17,7411 Å).

Під час дослідження фазових рівноваг у системі Sc–Co–In при 870 К виявлено утворення твердого розчину Sc₁₁Co₂In₃, (x=0–0,26, структурний тип MgCu₂, просторова група Fd-3m).

Методом електродугового плавлення у атмосфері чистого аргону синтезовано три зразки при складах: Sc₂Co₁₀In₁₃, Sc₂Co₉In₁₁₃ та Sc₁₆Co₉In₁₈₆. Твердий розчин досліджували рентгенівськими дифракційними методами порошку (дифрактометр Stoe IPDS, випромінювання CuKα) та монохристалл (чотирикутний дифрактометр Oxford Diffraction з детектором CCD Atlas, випромінювання MoKα), а також методом EDX аналізу (растворний електронний мікроскоп з рентгенівським мікраналізатором REMMA–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 – ScCoIn), Sc_{23}Co_{68}In_{9} (твердий розчин на основі ScCo) та Sc_{25}Co_{30}In_{44} (невідома сполука). Фазу Sc_{23}Co_{68}In_{9} ≡ Sc_{0.74}Co_{2}In_{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_{2}In_{0.04} (a = 6,91154(10) Å, Z = 8, R_{1} = 0,0167, wR_{2} = 0,0441) і Sc_{0.78}Co_{2}In_{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_{3}In_{0.24}, Dy_{1-0.90}Ni_{3}In_{0.90} та Tm_{1-0.50}Ni_{3}In_{0.50}. Однак у системі Er–Co–In твердий розчин (Er_{1-0.72}Co_{2}In_{0.28}) існує для структури типу PuNi_{3}.

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

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