**Chemistry of Metals and Alloys**

*Chem. Met. Alloys* 1 (2008) 317-322
Ivan Franko National University of Lviv
www.chemetal-journal.org

# Synthesis and crystal structure of the $La_6Co_{13}In$, $La_{5-\delta}Co_xIn_{3-x}$ and $La_3Co_xIn_{1-x}$ compounds

Mykola PUSTOVOYCHENKO[1], Mykola MANYAKO[1], Volodymyr PAVLYUK[1], Bernard MARCINIAK[2], Yaroslav KALYCHAK[1]*

[1] *Faculty of Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St.6, 79005 Lviv, Ukraine*
[2] *Institute of Chemistry and Environment Protection, Jan Dlugosz University of Czestochowa, Al. Armii Krajowej, 13/15, 42-200 Czestochowa, Poland*
* *Corresponding author. Tel.: +38-032-2600389; e-mail: kalychak@franko.lviv.ua*

Received October 6, 2008; accepted December 10, 2008; available on-line March 19, 2009

**In this work we report the synthesis and crystal structure of the compounds $La_6Co_{13}In$, $La_{5-\delta}Co_xIn_{3-x}$ and $La_3Co_xIn_{1-x}$. From X-ray single crystal diffraction data: $La_6Co_{13}In$ crystallizes in the structure type of $Nd_6Fe_{13}Si$, *I*4/*mcm*, *Z* = 4, *a* = 8.1190(4), *c* = 23.7022(15) Å; $La_{5-\delta}Co_xIn_{3-x}$ in the tetragonal structure type of $W_5Si_3$, *I*4/*mcm*, *Z* = 4, *a* = 12.9644(3), *c* = 6.1553(2) Å at $\delta$ = 0.125(15) and *x* = 0.06(3), and *a* = 12.9976(5), *c* = 6.1229(7) Å at $\delta$ = 0.275(15) and *x* = 0.10(3); $La_3Co_xIn_{1-x}$ is the solid solution of Co in $La_3In$, which crystallizes in the cubic structure type of $Cu_3Au$, $Pm\bar{3}m$, *Z* = 1, *a* = 5.0762(1) Å at *x* = 0.05.**

**Intermetallic compounds / Crystal structure / Lanthanum / Cobalt / Indium**

## Introduction

Over the last years, investigations of the chemistry of solids of indium with rare-earth and transition metals have led to the discovery of new intermetallic compounds, many of which are of interest for solid state physics [1,2]. For example, $CeCoIn_5$ [3,4], $CeRhIn_5$, and $CeIrIn_5$ [5,6] belong to a special class of heavy-fermion materials that have considerably advanced the knowledge of the interplay between superconductivity and magnetism [7]. We have now continued our systematic investigations of the *RE*–*T*–In (*RE* = rare-earth metal, *T* = transition metal) systems and their compounds. In this paper we present results on the synthesis and crystal structure of some lanthanum-rich compounds with cobalt and indium. It is known that two tetragonal and one cubic ternary compounds exist in this system: $LaCoIn_5$ [8] ($HoCoGa_5$ structure type, space group *P*4/*mmm* [9]), $La_6Co_{13}In$ [10] ($Nd_6Fe_{13}Si$ structure type, space group *I*4/*mcm*) and cubic $La_{12}Co_6In$ [11] ($Sm_{12}Ni_6In$ structure type, space group $Im\bar{3}$ [11]). Atom coordinates have been refined only for the $LaCoIn_5$ compound [8].

## Experimental section

Metals of the purity: lanthanum 99.85 wt.%, cobalt 99.92 wt.%, and indium 99.99 wt.%, were used as starting materials for the synthesis. Alloys of the compositions $La_{30}Co_{65}In_5$, $La_{60}Co_{10}In_{30}$, $La_{55}Co_{20}In_{25}$, and $La_{65}Co_{10}In_{25}$ (defined from an investigation of the isothermal section of the La–Co–In system at 870 K) were prepared by arc-melting under an argon atmosphere of 0.7-0.8 atm. The argon was purified by melting titanium sponge. To ensure homogeneity, the alloys were re-melted twice. The weight losses were negligible. The alloys were wrapped into tantalum foil and sealed in evacuated silica tubes. The following heat treatment was performed: the samples were quickly heated to 1170 K, and after one hour the temperature was reduced by 10 K every 40 minutes until 1070 K. After two days at 1070 K, the temperature was reduced with the same rate down to 870 K. Then the samples were annealed at 870 K for 2 months, and finally quenched in cold water.

No reaction with tantalum was observed and on the surface of the specimens irregularly shaped single crystals had formed. The single crystals were selected by mechanical fragmentation and were investigated by Laue photographs and the rotation method (Mo Kα radiation) in order to check their quality for the intensity data collection, symmetry and lattice constants. Intensity data were measured at room temperature on a Xcalibur diffractometer with a charge-coupled device (CCD) detector. The crystallographic data and details of the data collection are listed in Table 1. The single crystals investigated on the diffractometer were also studied by energy

**Table 1** Crystal data and structure refinement of $La_6Co_{13}In$ (I), $La_{4.875}Co_{0.06}In_{2.94}$ (IIA), $La_{4.725}Co_{0.10}In_{2.90}$ (IIB), and $La_3Co_{0.05}In_{0.95}$ (III).

| | $La_6Co_{13}In$ | $La_{4.875}Co_{0.06}In_{2.94}$ | $La_{4.725}Co_{0.10}In_{2.90}$ | $La_3Co_{0.05}In_{0.95}$ |
|---|---|---|---|---|
| Molar mass | 1714.409 | 1018.293 | 995.221 | 528.74 |
| Crystal system | tetragonal | tetragonal | tetragonal | cubic |
| Space group | *I*4/*mcm* | *I*4/*mcm* | *I*4/*mcm* | *Pm*$\bar{3}$*m* |
| Pearson symbol | *tI*80 | *tI*31.50 | *tI*30.90 | *cP*4 |
| Unit cell dimension (*a*, Å) | 8.1190(4) | 12.9644(3) | 12.9976(5) | 5.07620(10) |
| Unit cell dimension (*c*, Å) | 23.7022(15) | 6.1533(2) | 6.1229(7) | 5.07620(10) |
| Unit cell volume (*V*, Å$^3$) | 1562.41(15) | 1034.22(5) | 1034.39(13) | 130.803(4) |
| Formula units per cell | 4 | 4 | 4 | 1 |
| Calculated density (g/cm$^3$) | 7.2885 | 6.5400 | 6.3908 | 6.7481 |
| Crystal size (μm$^3$) | ~120×80×15 | ~250×100×15 | ~250×100×15 | ~200×150×30 |
| Absorption coefficient (mm$^{-1}$) | 20.522 | 25.853 | 25.241 | 30.642 |
| F(000) | 2128 | 1659 | 1622 | 266 |
| θ range for data collection | 3.44 - 26.34 | 2.22 - 26.37 | 2.22 - 26.28 | 4.01 - 26.28 |
| Range in *hkl* | -8≤*h*≤10 | -16≤*h*≤16 | -16≤*h*≤15 | -6≤*h*≤5 |
| | -10≤*k*≤8 | -15≤*k*≤16 | -16≤*k*≤16 | -4≤*k*≤6 |
| | -29≤*l*≤29 | -6≤*l*≤7 | -7≤*l*≤7 | -6≤*l*≤6 |
| Total no. reflections | 4698 | 3115 | 3171 | 424 |
| Independent reflections | 457 | 313 | 312 | 45 |
| Reflections with I>2σ(I) | 418 | 288 | 248 | 25 |
| Data/parameters | 418/34 | 288/18 | 248/16 | 25/5 |
| Goodness-of-fit on F$^2$ | 1.230 | 1.058 | 1.110 | 1.082 |
| R [I>2σ(I)] (R1=) | 0.0177 | 0.0478 | 0.0498 | 0.0365 |
| R [I>2σ(I)] (wR2=) | 0.0382 | 0.1239 | 0.1231 | 0.0989 |
| R [all] (R1=) | 0.0208 | 0.0509 | 0.0640 | 0.0528 |
| R [all] (wR2=) | 0.0401 | 0.1268 | 0.1329 | 0.1123 |
| Extinction coefficient | 0.00038(3) | 0.00032(14) | - | 0.023(9) |
| Largest diff. peak and hole | 1.108/-0.962 | 6.374/-3.358 | 3.548/-4.014 | 8.471/-1.651 |

dispersive X-ray analysis (EDX), using a Leica420i scanning electron microscope.

## Results and discussion

The experimentally observed compositions from EDX analysis are: 31.28% La, 63.25% Co, and 5.46% In for crystal I from the $La_{30}Co_{65}In_5$ alloy; 56.54% La, 8.34% Co, and 35.12% In for crystal IIA from the $La_{60}Co_{10}In_{30}$ alloy, and 55.45% La, 8.81% Co, and 35.74% In for crystals IIB from the $La_{55}Co_{20}In_{25}$ alloy (Fig. 1). We selected two crystals of compound II for the crystal structure investigation because they had slightly different chemical compositions. The single crystal III was selected from the $La_{65}Co_{10}In_{25}$ alloy. The diffractometer data confirmed the symmetry and lattice constants obtained by the photographic method. Starting atomic parameters were deduced from automatic interpretations of direct methods with SHELXS-97 [12], and the structures were refined using SHELXL-97 [12] with anisotropic atomic displacement parameters. The results of the crystal structure refinements are presented in Tables 2 and 3 and in Figs. 2 through 4. The refinement readily revealed isotypism of the crystal I with the $Nd_6Fe_{13}Si$ [13] (= $La_6Co_{11}Ga_3$ [14]) structure type, crystals IIA and IIB with the $W_5Si_3$ structure type [15], and III with the $Cu_3Au$ structure type [15].

In the case of the compound $La_6Co_{13}In$ (Fig. 2), the cell parameters correlate well with literature data [10], and all the atomic positions are occupied completely. The coordination polyhedra of the

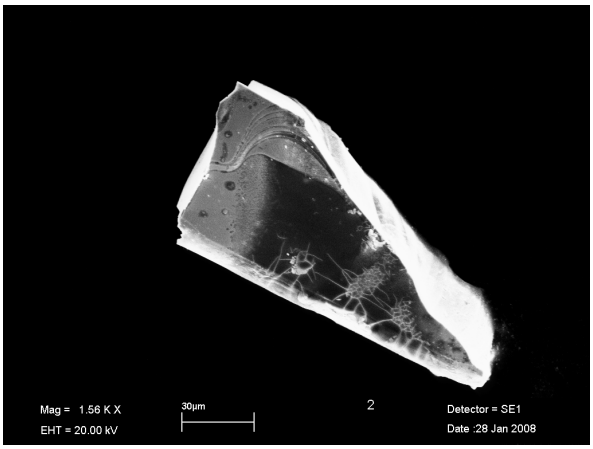


**Fig. 1** Single crystal of the $La_{5-\delta}Co_xIn_{3-x}$ compound.

**Table 2** Atomic coordinates, site occupations (*G*), and equivalent isotropic displacement parameters ($U_{eq}$, Å$^2$) for $La_6Co_{13}In$ (I), $La_{4.875}Co_{0.06}In_{2.94}$ (IIA), $La_{4.725}Co_{0.10}In_{2.90}$ (IIB), and $La_3Co_{0.05}In_{0.95}$ (III).

| Atom | Wyckoff site | *x* | *y* | *z* | *G* | $U_{eq}$ |
|---|---|---|---|---|---|---|
| | | | $La_6Co_{13}In$ | | | |
| La1 | 16*l* | 0.33752(4) | 0.16248(4) | 0.31860(2) | 1 | 0.0133(2) |
| La2 | 8*f* | 0 | 0 | 0.39880(2) | 1 | 0.0093(2) |
| Co1 | 16*l* | 0.32220(8) | 0.17780(8) | 0.44472(4) | 1 | 0.0082(2) |
| Co2 | 16*k* | 0.0644(1) | 0.2121(1) | 1/2 | 1 | 0.0084(2) |
| Co3 | 16*l* | 0.11331(8) | 0.38669(8) | 0.41217(4) | 1 | 0.0089(2) |
| Co4 | 4*d* | 0 | 1/2 | 1/2 | 1 | 0.0068(4) |
| In | 4*a* | 0 | 0 | 1/4 | 1 | 0.0112(2) |
| | | | $La_{4.875}Co_{0.06}In_{2.94}$ | | | |
| La1 | 4*b* | 0 | 1/2 | 3/4 | 0.88(2) | 0.057(2) |
| La2 | 16*k* | 0.0828(1) | 0.2211(1) | 0 | 1 | 0.0247(6) |
| In1 | 4*a* | 0 | 0 | 1/4 | 1 | 0.0222(8) |
| In2 | 8*h* | 0.3369(1) | 0.1631(1) | 0 | 0.97(3) | 0.024(1) |
| Co | 8*h* | 0.3369(1) | 0.1631(1) | 0 | 0.03(3) | 0.024(1) |
| | | | $La_{4.725}Co_{0.10}In_{2.90}$ | | | |
| La1 | 4*b* | 0 | 1/2 | 3/4 | 0.73(2) | 0.067(3) |
| La2 | 16*k* | 0.0823(1) | 0.22162(11) | 0 | 1 | 0.0298(6) |
| In1 | 4*a* | 0 | 0 | 1/4 | 1 | 0.0265(9) |
| In2 | 8*h* | 0.3363(1) | 0.1637(1) | 0 | 0.95(3) | 0.029(1) |
| Co | 8*h* | 0.3363(1) | 0.1637(1) | 0 | 0.05(3) | 0.029(1) |
| | | | $La_3Co_{0.05}In_{0.95}$ | | | |
| La | 3*d* | 0 | 1/2 | 0 | 1 | 0.0134(8) |
| Co | 1*b* | 1/2 | 1/2 | 1/2 | 0.05(5) | 0.009 |
| In | 1*b* | 1/2 | 1/2 | 1/2 | 0.95(5) | 0.009 |

**Table 3** Anisotropic displacement parameters (Å$^2$) of $La_6Co_{13}In$ (I), $La_{4.875}Co_{0.06}In_{2.94}$ (IIA), $La_{4.725}Co_{0.10}In_{2.90}$ (IIB), and $La_3Co_{0.05}In_{0.95}$ (III).

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| | | | $La_6Co_{13}In$ | | | |
| La1 | 0.0144(2) | 0.0144(2) | 0.0111(2) | 0.0003(1) | -0.0003(1) | -0.0022(2) |
| La2 | 0.0100(2) | 0.0100(2) | 0.0080(3) | 0 | 0 | 0 |
| Co1 | 0.0067(5) | 0.0067(5) | 0.0070(8) | 0 | 0 | -0.0011(7) |
| Co2 | 0.0071(4) | 0.0088(5) | 0.0092(4) | 0 | 0 | 0.0005(3) |
| Co3 | 0.0081(3) | 0.0081(3) | 0.0082(4) | 0.0001(3) | -0.0001(3) | 0.0001(3) |
| Co4 | 0.0092(3) | 0.0092(3) | 0.0085(5) | -0.0003(3) | 0.0003(3) | -0.0001(3) |
| In | 0.0123(3) | 0.0123(3) | 0.0091(5) | 0 | 0 | 0 |
| | | | $La_{4.875}Co_{0.06}In_{2.94}$ | | | |
| La1 | 0.0192(8) | 0.0199(8) | 0.0351(9) | 0 | 0 | -0.0021(5) |
| La2 | 0.0214(14) | 0.0214(14) | 0.127(5) | 0 | 0 | 0 |
| In | 0.0193(10) | 0.0193(10) | 0.0280(16) | 0 | 0 | 0 |
| | | | $La_{4.725}Co_{0.10}In_{2.90}$ | | | |
| La1 | 0.0294(9) | 0.029(1) | 0.031(1) | 0 | 0 | -0.0027(6) |
| La2 | 0.021(2) | 0.021(2) | 0.160(7) | 0 | 0 | 0 |
| In | 0.027(1) | 0.0267(1) | 0.026(2) | 0 | 0 | 0 |
| | | | $La_3Co_{0.05}In_{0.95}$ | | | |
| La | 0.014(2) | 0.012(2) | 0.014(2) | 0 | 0 | 0 |

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

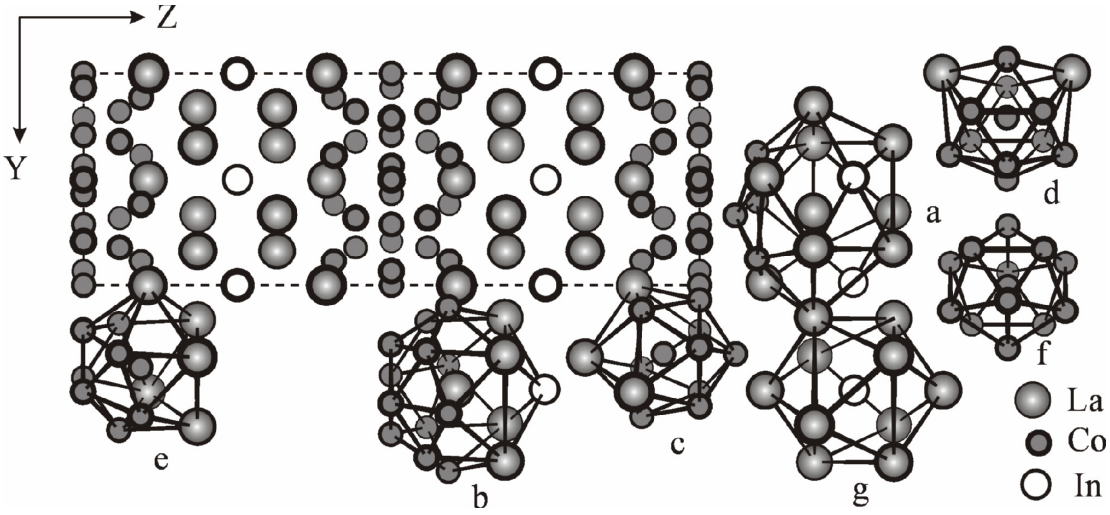


**Fig. 2** Projection of the structure of $La_6Co_{13}In$ on the YZ-plane and coordination polyhedra of the atoms: La (a,b), Co (c,d,e,f), In (g).

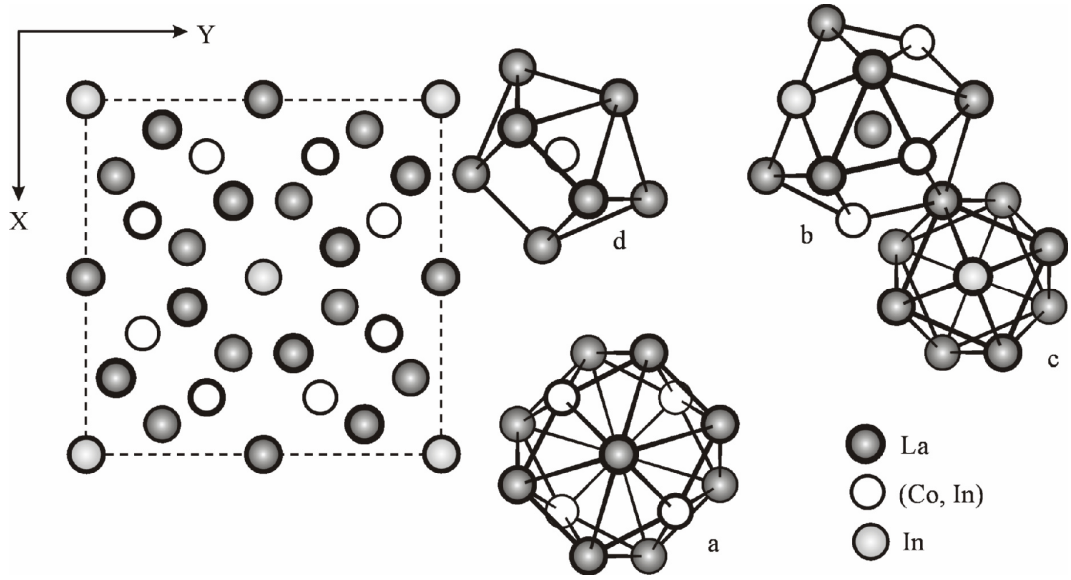


**Fig. 3** Projection of the structure of $La_{5-\delta}Co_xIn_{3-x}$ on the XY-plane and coordination polyhedra of the atoms: La (a,b), (Co,In) (d), In (c).

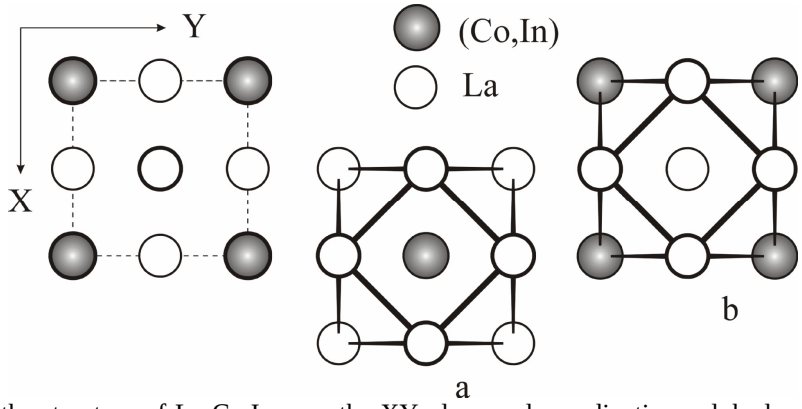


**Fig. 4** Projection of the structure of $La_3Co_xIn_{1-x}$ on the XY-plane and coordination polyhedra of the atoms: La (b), (Co,In) (a).

lanthanum atoms are pentacapped pentagonal prisms with one (coordination number (CN = 16 for La1) or two (CN = 17 for La2) capped bases. The coordination polyhedra of the cobalt atoms are distorted icosahedra (CN = 12), and those of the indium atoms are tetragonal antiprisms with capped bases (CN = 10). Compounds with the $Nd_6Fe_{13}Si$ structure type are formed only for the light lanthanides when the transition metal is Fe (*RE* = Pr, Nd, Sm) [16]. The peculiarity of $La_6Co_{13}In$ is the small amount of In and its unusual coordination polyhedron. For other $RE_xT_yIn_z$ compounds with similar composition the coordination polyhedra of the indium atoms are derivatives of icosahedra or cuboctahedra. The structure type $Nd_6Fe_{13}Si$, like the closely related type $La_6Co_{11}Ga_3$, is an intergrowth structure, which consists of $YNi_9In_2$- [17] and $Cr_5B_3$-type slabs in the ratio 2:1. In turn, the $YNi_9In_2$ structure is an intergrowth of the simpler types $Zr_4Al_3$ and $CeMg_2Si_2$ in the ratio 2:2, and the structure $Cr_5B_3$ is an intergrowth of the types $CuAl_2$ and $U_3Si_2$ in the ratio 1:2. The $U_3Si_2$ type itself consists of CsCl- and $AlB_2$-related slabs [1].

The refinements of the IIA and IIB crystals, which belong to the $W_5Si_3$ type (Fig. 3), are satisfactory only when defects in position 4*b*, occupied by La atoms, and a statistical mixture of Co and In atoms in position 8*h* are accounted for (Table 2). The degree of defects is different for the IIA and IIB crystals and the composition of the statistical mixture also differs. This leads to the conclusion that a certain homogeneity range exists for this compound. For the La1 atoms, the coordination polyhedra are distorted hexagonal antiprisms with capped bases (CN = 14), and for the La2 atoms polyhedra with 15 vertices (CN = 15). The indium atoms are situated at the centers of tetragonal antiprisms with capped bases (CN = 10), and the statistical mixture (Co,In)2 in defect icosahedra (CN = 10). Ternary compounds of the $W_5Si_3$ structure type in the *RE*–*T*–In systems are found for the first time. Binary compounds with the $RE_5In_3$ composition exist in *RE*–In systems of rare-earth metals of the yttrium subgroup (*RE* = Y, Gd, Tb, Dy, Ho, Er, Tm, Lu). It is also known that for *RE* = Gd, Tb, Dy they belong to the $W_5Si_3$ type and for *RE* = Er, Tm, Lu, Y they have the hexagonal $Mn_5Si_3$ structure type. The compound $Ho_5In_3$ has two modifications: a low-temperature modification with the $Mn_5Si_3$ structure type and a high-temperature modification with the $W_5Si_3$ structure type. The $La_{5-\delta}Co_xIn_{3-x}$ compound is the binary "$La_5In_3$" compound, which does not exist without Co additions, likely stabilized by Co atoms.

The presence of a statistical mixture of Co and In atoms is also characteristic for the compound III ($La_3Co_{0.05}In_{0.95}$) with $Cu_3Au$ structure type, which is a solid solution with a small (about 1 at.%) solubility of Co in the $La_3In$ compound.

For all of the compounds investigated in this paper the interatomic distances are close to the sum of atomic radii. A single exception is the distance in the $La_{5-\delta}Co_xIn_{3-x}$ compounds between the atoms La1 in the [001] direction. It is equal to half of the lattice constant *c*, i.e. 3.0766(1) (17.6%) for the IIA and 3.0614(2) Å (18.1%) IIB crystals, respectively.

## Conclusions

1. The crystal structures of the ternary compounds $La_6Co_{13}In$, $La_{5-\delta}Co_xIn_{3-x}$ and $La_3Co_xIn_{1-x}$ have been studied by means of X-ray single crystal diffraction.
2. $La_6Co_{13}In$ belongs to the closely related structure types $Nd_6Fe_{13}Si$ and $La_6Co_{11}Ga_3$.
3. The results of the refinements of the $La_{5-\delta}Co_xIn_{3-x}$ compound ($La_{4.875}Co_{0.06}In_{2.94}$, $La_{4.725}Co_{0.10}In_{2.90}$) which belongs to the $W_5Si_3$ type, are satisfactory only when defects in position 4*b* (site La1) and a statistical mixture of Co and In atoms in position 8*h* are accounted for.
4. $La_3Co_xIn_{1-x}$ ($x$ = 0.05) is the solid solution of Co in the $La_3In$ compound, which crystallizes in the cubic structure type $Cu_3Au$.

## References


[1] Ya.M. Kalychak, V.I. Zaremba, R. Pöttgen, M. Lukachuk, R.-D. Hoffmann, In: K.A. Gschneidner Jr., V.K. Pecharsky, J.-C. Bünzli (Eds.), *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 34, Ch. 218, Elsevier, Amsterdam, 2005, pp. 1-133.

[2] P. Thalmeier, G. Zwicknagl, In: K.A. Gschneidner Jr., V.K. Pecharsky, J.-C. Bünzli (Eds.), *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 34, Chapter 219, Elsevier, Amsterdam, 2005, pp. 135-287.

[3] Ya.M. Kalychak, *Visn. Lviv. Univ., Ser. Khim.* 38 (1999) 70.

[4] Ya.M. Kalychak, V.I. Zaremba, V.M. Baranyak, V.A. Bruskov, P.Yu. Zavalij, *Izv. Akad. Nauk SSSR, Met.* 1 (1989) 209.

[5] E.G. Moshopoulou, Z. Fisk, J.L. Sarrao, J.D. Thompson, *J. Solid State Chem.* 158 (2001) 25.

[6] J.D. Thompson, R. Movshovich, Z. Fisk, F. Bouquet, N.J. Curro, R.A. Fisher, P.C. Hammel, H. Hegger, M.F. Hundley, M. Jaime, P.G. Pagliuso, C. Petrovic, N.E. Phillips, J.L. Sarrao, *J. Magn. Magn. Mater.* 226-230 (2001) 5.

[7] H.J. Curro, T. Coldwell, E.D. Bauer, L.A. Morales, M.J. Grat, Y. Bang, A.V. Balatsky, J.D. Thompson, J.L. Sarrao, *Nature* 434 (2005) 622.

[8] R.T. Macaluso, J.L. Sarrao, P.G. Pagliuso, V.O. Moreno, R.G. Goodrich, D.A. Browne,

F.R. Fronczek, J.Y. Chan, *J. Solid State Chem.* 166 (2002) 245.
[9] Yu.N. Grin, Ya.P. Yarmolyuk, E.I. Gladyshevskii, *Kristallografia* 29 (1979) 242.
[10] F. Weitzer, A. Leithe-Jasper, P. Rogl, K. Hiebl, H. Noël, G. Wiesinger, W. Steiner, *J. Solid State Chem.* 104 (1993) 368.
[11] Ya.M. Kalychak, V.I. Zaremba, A. Stepien-Damm, Ya.V. Galadzhun, L.G. Akselrud, *Kristallografia* 43 (1998) 17.
[12] G.M. Sheldrick, *SHELX-97*, University of Göttingen, Germany, 1997.
[13] J. Allemand, A. Letant, J.M. Moreau, J.P. Nozieres, R. Perrier de la Bathie, *J. Less-Common Met.* 166 (1990) 73.
[14] O.M. Sichevych, R.V. Lapunova, A.N. Sobolev., Yu.N. Grin, Ya.P. Yarmolyuk, *Kristallografia* 30 (1985) 1077.
[15] P. Villars, L.D. Calvert (Eds.), *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, American Society for Metals, OH, Vols. 1-3, 1985, 6087 p.
[16] F. Weitzer, P. Rogl, *J. Less-Common Met.* 167 (1990) 135.
[17] Ya.M. Kalychak, L.G. Akselrud, V.I. Zaremba, V.M. Baranyak, *Dopov. Akad. Nauk. Ukr. RSR* 8 (1984) 37.