Journal of Solid State Chemistry 181 (2008) 3223–3228

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Structure and magnetic properties of RE_2CuIn_3 (RE = Ce, Pr, Nd, Sm and Gd)

Yuriy B. Tyvanchuk [a], Andrzej Szytuła [b], Arkadiusz Zarzycki [b], Ute Ch. Rodewald [c], Yaroslav M. Kalychak [a], Rainer Pöttgen [c,*]

[a] Faculty of Chemistry, Ivan Franko National University of Lviv, Kyryla and Mephodiya Street 6, 79005 Lviv, Ukraine
[b] Marian Smoluchowski Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Kraków, Poland
[c] Institut für Anorganische und Analytische Chemie, Universität Münster, Corrensstrasse 30, D-48149 Münster, Germany

ARTICLE INFO

Article history:
Received 16 June 2008
Received in revised form
12 August 2008
Accepted 17 August 2008
Available online 23 August 2008

Keywords:
Indium
Intermetallics
Crystal chemistry
Magnetism

ABSTRACT

The ternary copper indides $RE_2CuIn_3 \equiv RECu_{0.5}In_{1.5}$ (RE = Ce, Pr, Nd, Sm and Gd) were synthesized from the elements in sealed tantalum tubes in an induction furnace. They crystallize with the $CaIn_2$-type structure, space group $P6_3/mmc$, with a statistical occupancy of copper and indium on the tetrahedral substructure. These indides show homogeneity ranges $RECu_xIn_{2-x}$. Single crystal structure refinements were performed for five crystals: $CeCu_{0.66}In_{1.34}$ ($a = 479.90(7)$ pm, $c = 768.12(15)$ pm), $PrCu_{0.52}In_{1.48}$ ($a = 480.23(7)$ pm, $c = 759.23(15)$ pm), $NdCu_{0.53}In_{1.47}$ ($a = 477.51(7)$ pm, $c = 756.37(15)$ pm), $SmCu_{0.46}In_{1.54}$ ($a = 475.31(7)$ pm, $c = 744.77(15)$ pm), and $GdCu_{0.33}In_{1.67}$ ($a = 474.19(7)$, $c = 737.67(15)$ pm). Temperature-dependent susceptibility measurements show antiferromagnetic ordering at $T_N = 4.7$ K for Pr_2CuIn_3 and Nd_2CuIn_3 and 15 K for Sm_2CuIn_3. Fitting of the susceptibility data of the samarium compound revealed an energy gap $\Delta E = 39.7(7)$ K between the ground and the first excited levels.

1. Introduction

The rare-earth metal (RE)–transition metal (T)–indium systems have intensively been studied in the last 30 years with respect to the crystal chemical peculiarities and interesting magnetic properties [1–3]. Of the many RE–T–In systems, those with copper have most thoroughly been studied with respect to phase analyses. Several isothermal sections have been completely analysed [4].

Except scandium, ytterbium, and lutetium, the RE–Cu–In systems show extended solid solutions $RECu_xIn_{2-x}$ [5–10] with AlB_2-related structures. During the first studies at 873 K [5–8], a small AlB_2-related cell with a statistical distribution of the copper and indium atoms on the boron network was assumed based on powder diffraction data. Later on doubling of the subcell c-axis was observed, pointing to a $CaIn_2$-related structure. In general, ordering variants for such solid solutions RET_xX_{2-x} (X = element of the third, fourth, or fifth main group) with AlB_2-related structures have been observed for the compositions $RETX$ and $RET_{0.5}X_{1.5}$ (i.e. RE_2TX_3). The crystal chemical peculiarities and the group–subgroup relations starting from the aristotype AlB_2 have recently been reviewed [11]. In view of these systematic studies on the AlB_2 superstructures we have reinvestigated the $RECu_xIn_{2-x}$ systems for $x = 0.5$. Herein we report on single crystal studies and magnetic properties.

2. Experimental

2.1. Synthesis

Starting materials for the preparation of the RE_2CuIn_3 samples were ingots of the rare-earth elements (Johnson Matthey, Chempur or Kelpin), copper drops (Heraeus), and indium tear drops (Heraeus), all with stated purities better than 99.9%. In a first step the rare-earth ingots ware mechanically cut into smaller pieces and arc-melted to small buttons under an atmosphere of about 600 mbar argon in a water-cooled copper crucible [12]. The argon was purified with silica gel, molecular sieves, and titanium sponge (900 K). The pre-melting procedure strongly reduces a shattering of the elements during the strongly exothermic reaction with copper and indium.

The starting components were weighed in the atomic ratio 2:1:3 and arc-welded in small tantalum tubes under an argon pressure of about 600 mbar. The tubes were then placed in a water-cooled sample chamber [13] of a high-frequency furnace (Hüttinger Elektronik, Freiburg, Type TIG 5/300) and first heated under flowing argon with the maximum power of the generator. The exothermic reaction between the three elements was visible by the occurrence of a heat flash near ~1500 K. After 5 min the

* Corresponding author. Fax: +49 251 83 36002.
E-mail addresses: yutyv@franko.lviv.ua (Y.B. Tyvanchuk), pottgen@uni-muenster.de (R. Pöttgen).

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doi:10.1016/j.jssc.2008.08.020

Table 1
Crystallographic data and lattice parameters of the ternary RE_2CuIn_3 compounds (RE = Ce–Nd, Sm and Gd

Starting composition	Refined composition	Str. type	SG	a (pm)	c (pm)	Reference
$CeCu_{0.5}In_{1.5}$		AlB_2	$P6/mmm$	481.8(1)	389.9(1)	[1]
Ce_2CuIn_3		AlB_2	$P6/mmm$	482.1	385.2	[6]
2Ce:Cu:3In[a]		$CaIn_2$	$P6_3/mmc$	482.2(3)	763.3(3)	This work
	$CeCu_{0.66(2)}In_{1.34(2)}$[b]	$CaIn_2$	$P6_3/mmc$	479.90(7)	768.12(15)	This work
$CeCu_{0.8-0.4}In_{1.2-1.6}$		AlB_2	$P6/mmm$	480.4–483.5(1)	383.7–391.7(2)	[1]
$PrCu_{0.5}In_{1.5}$		AlB_2	$P6/mmm$	478.9(2)	381.2(3)	[1]
Pr_2CuIn_3		AlB_2	$P6/mmm$	480.8	386.0	[6]
2Pr:Cu:3In[a]		$CaIn_2$	$P6_3/mmc$	479.7(3)	758.5(3)	This work
	$PrCu_{0.52(2)}In_{1.48(2)}$[b]	$CaIn_2$	$P6_3/mmc$	480.23(7)	759.23(15)	This work
$PrCu_{0.5-0.2}In_{1.5-1.8}$		AlB_2	$P6/mmm$	478.2–485.3	395.8–378.9	[1]
$NdCu_{0.5}In_{1.5}$		AlB_2	$P6/mmm$	478.4(1)	380.0(2)	[1]
Nd_2CuIn_3		AlB_2	$P6/mmm$	482.1	380.9	[6]
2Nd:Cu:3In[a]		$CaIn_2$	$P6_3/mmc$	478.9(2)	752.6(2)	This work
	$NdCu_{0.53(2)}In_{1.47(2)}$[b]	$CaIn_2$	$P6_3/mmc$	477.51(7)	756.37(15)	This work
$NdCu_{0.7-0.3}In_{1.3-1.7}$		AlB_2	$P6/mmm$	477.3–481.3(1)	376.4–380.5(2)	[1]
2Sm:Cu:3In[a]		$CaIn_2$	$P6_3/mmc$	475.6(2)	743.9(2)	This work
	$SmCu_{0.46(2)}In_{1.54(2)}$[b]	$CaIn_2$	$P6_3/mmc$	475.31(7)	744.77(15)	This work
$SmCu_{0.5}In_{1.5}$		AlB_2	$P6/mmm$	470.4(1)	364.7(1)	[1]
$SmCu_{0.6-0.2}In_{1.4-1.8}$		AlB_2	$P6/mmm$	474.7–481.3(1)	372.5–369.9(1)	[1]
2Gd:Cu:3In[a]		$CaIn_2$	$P6_3/mmc$	474.4(2)	737.9(2)	This work
	$GdCu_{0.33(3)}In_{1.67(3)}$[b]	$CaIn_2$	$P6_3/mmc$	474.19(7)	737.67(15)	This work
$GdCu_{0.59-0.35}In_{1.41-1.65}$		AlB_2	$P6/mmm$	473.0–477.0(1)	369.2–367.5(1)	[1]
Gd_2CuIn_3		$CaIn_2$	$P6_3/mmc$	474.09(9)	738.57(9)	[9]

[a] Lattice parameters from Guinier powder data.
[b] Lattice parameters from diffractometer measurements.

temperature was slowly decreased in order to enhance the growth of small single crystals. At 900 K the tube was annealed for another 2 h followed by quenching, resulting in polycrystalline samples of RE_2CuIn_3. The compounds are stable in air over weeks. Single crystals exhibit metallic luster while ground powders are dark grey.

2.2. X-ray powder data

The RE_2CuIn_3 samples were characterized by Guinier powder diagrams using Cu$K\alpha_1$ radiation and α-quartz ($a = 491.30$ pm and $c = 540.46$ pm) as an internal standard. The Guinier camera was equipped with an imaging plate system (Fujifilm, BAS-1800). The hexagonal lattice parameters (Table 1) were obtained by least-squares refinements. The correct indexing was ensured by a comparison with calculated patterns [14]. The powder patterns clearly revealed the superstructure reflections for doubling of the c-axis of the AlB_2-related subcells.

2.3. Single crystal X-ray diffraction

Irregularly shaped crystals of RE_2CuIn_3 (RE = Ce, Pr, Nd, Sm, Gd) samples were directly selected from the crushed annealed samples. The crystals were glued to small quartz fibres using varnish and first checked by Laue photographs on a Buerger camera, equipped with the same Fujifilm, BAS-1800 imaging plate technique. Intensity data were collected on a Stoe IPDS II diffractometer (graphite monochromatized Mo$K\alpha$ radiation; oscillation mode) and numerical absorption corrections were applied to the data sets. All relevant crystallographic data for the data collections and evaluations are listed in Table 2.

2.4. Scanning electron microscopy

The single crystals investigated on the diffractometer and the bulk samples were analysed using a Leica 420 I scanning electron microscope with CeO_2, the rare-earth trifluorides, copper, and InAs as standards. No impurity elements heavier than sodium (detection limit of the instrument) were observed. The compositions determined semi-quantitatively by EDX were close to the ideal one.

2.5. Magnetic measurements

DC magnetic measurements of X-ray pure samples of Pr_2CuIn_3, Nd_2CuIn_3, and Sm_2CuIn_3 were carried out using a commercial MPMS SQUID magnetometer. Two types of measurements were performed: magnetic susceptibility measurements in a magnetic field of 1 kOe in the temperature range 2–300 K (from these data the effective magnetic moment μ_{eff} and the paramagnetic Curie temperature θ_p were obtained) and magnetization measurements in magnetic fields up to 50 kOe at about 2 K (in order to get the value of the pseudo-saturated magnetic moment and the character of the magnetization curve). Since the crystallites had not well-defined shapes, no demagnetization effects were taken into account.

3. Results and discussion

3.1. Structure refinements

Careful analyses of the diffractometer data sets clearly revealed the doubling of the subcell c-axis and the reflection conditions were compatible with space group $P6_3/mmc$. The atomic parameters of Tb_2CuIn_3 [10] were taken as starting values and the structures were refined with anisotropic displacement parameters for all atoms with SHELXL-97 (full-matrix least-squares on F_o^2) [15]. The 4f site was refined with mixed Cu/In occupancy for all crystals, leading to the compositions listed in Table 2. Final difference Fourier syntheses revealed no significant residual peaks. The refinements then converged to the residuals listed in Table 2 and the atomic parameters and interatomic distances listed in Tables 3 and 4 (distances exemplarily for