Investigation of the interaction of the components in the $RE_{1-x}RE'_xCu_2In$ (RE = Y, La, Ce, Gd) systems

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Four pseudo-binary $RE_{1-x}RE'_xCu_2In$ systems were investigated at 870 K using X-ray diffraction: $(La,Y)Cu_2In$, $(La,Ce)Cu_2In$, $(La,Gd)Cu_2In$, and $(Y,Gd)Cu_2In$. The formation of continuous solid solutions with $MnCu_2Al$-type structure was observed in all cases. In agreement with the atomic radii of the rare-earth elements, the composition dependencies of the unit cell parameters of these Heusler phases exhibit a monotonous decrease when La is replaced by Y, Ce, or Gd, but a slight increase when Y is replaced by Gd. An investigation of the magnetic properties of single-phase alloys belonging to the $La_{1-x}Gd_xCu_2In$ solid solution (x = 0.1-0.4) showed Curie-Weiss paramagnetism with predominantly antiferromagnetic interactions between Gd^{3+} ions, but no magnetic ordering down to 1.72 K.

Ternary indides / Solid solution / X-ray powder diffraction

Introduction

The intermetallic compounds $RECu_2In$ (RE = rare earth, Y, Sc) represent a considerable part of all known ternary indides $RE_xCu_yIn_z$ [1]. These compounds crystallize with $MnCu_2Al$-type structures (space group $Fm\text{-}3m$) [2] and belong to the rich family of Heusler phases. This family includes isostructural copper indides of all the rare-earth metals, with two exceptions, namely Eu and Yb [3,4]. No significant homogeneity range has been reported for any of these compounds.

The physical properties of these materials have been intensively studied. The $CeCu_2In$ compound was found to exhibit large electronic contributions to the specific heat ($C/T = 1200$ mJ/mol·K^2 below $T = 1.4$ K), which is a common feature for heavy-fermion materials [5-7]. The $GdCu_2In$ compound was reported to order antiferromagnetically below $T_N = 9.6$ K [8].

The influence of substitution by other elements on the physical properties and structural features of a number of systems based on the aforementioned compounds has studied. In the $CeCu_{2-x}Ag_xIn$ system, a continuous solid solution is formed when copper is replaced by silver [5]. Despite this fact, a significant change in the physical properties is observed: from heavy-fermion behavior in $CeCu_2In$, to antiferromagnetic order in $CeAg_2In$. Unlimited solubility and formation of continuous solid solutions were also found in the $Ce_{1-x}RE_xCu_2In$ (RE = La, Y) systems [7]. Substitution for In in $RECu_2In$ (RE = Y, La, Ce, Gd) compounds, results in the formation of narrow solid solutions, and the original cubic structure is only retained within a limited concentration range when aluminum is substituted for indium [9,10].

Here we report the results of investigations of four quasi-binary $RE_{1-x}RE'_xCu_2In$ systems: $(La,Y)Cu_2In$, $(La,Ce)Cu_2In$, $(La,Gd)Cu_2In$, and $(Y,Gd)Cu_2In$. The investigations included determination of the composition dependence of the unit cell parameters of the $MnCu_2Al$-type phase, and studies of the magnetic properties of $(La,Gd)Cu_2In$ samples.

Experimental

In order to study the $RE_{1-x}RE'_xCu_2In$ (RE = Y, La, Ce, Gd) systems, samples with a mass of up to 1 g were synthesized by arc-melting the constituent elements (purity of the main component at least 99.8 mass%) under purified argon atmosphere. Titanium sponge was used as a getter material. The total weight losses after melting were less than 0.75 % in all cases.

Therefore the composition was assumed to be equal to the nominal composition. Subsequent annealing of the samples was carried out in evacuated quartz tubes, held at 870 K for 720 h. Both the as cast and the annealed alloys, also in the form of powders, are stable in air.

The phase composition of the samples was analyzed on powder diffraction patterns recorded at room temperature on an automatic diffractometer PANalytical X'Pert Pro (Cu $K\alpha$ radiation). The unit cell parameters were determined and the crystal structure was refined using X'Pert HighScore and FullProf programs [11]. X-ray diffraction patterns of selected samples of the investigated systems, are shown on Fig. 1.
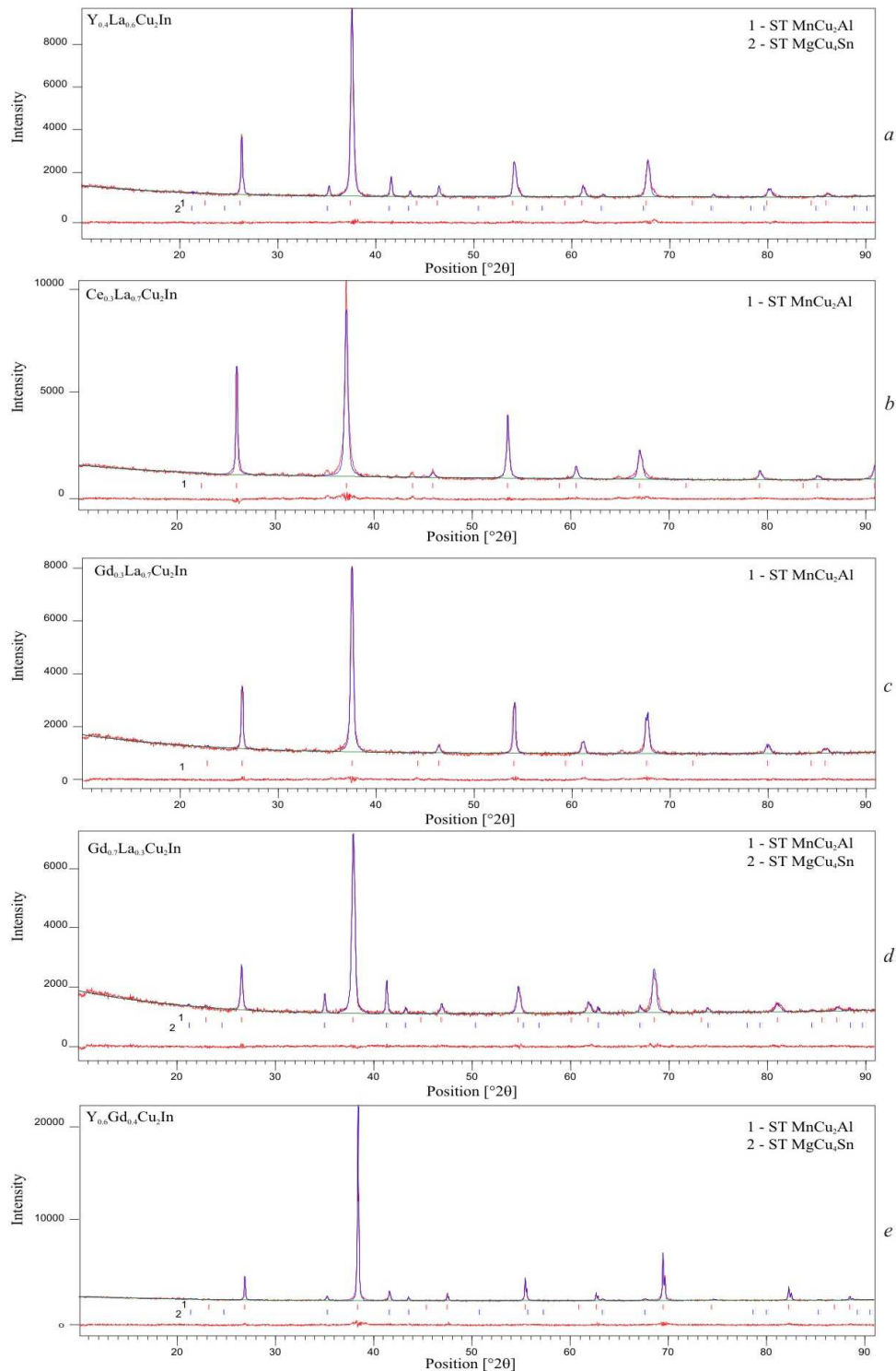

Fig. 1 X-ray diffraction patterns of $Y_{0.4}La_{0.6}Cu_2In$ (*a*), $Ce_{0.3}La_{0.7}Cu_2In$ (*b*), $La_{0.3}Gd_{0.7}Cu_2In$ (*c*), $La_{0.7}Gd_{0.3}Cu_2In$ (*d*), and $Y_{0.6}Gd_{0.4}Cu_2In$ (*e*).

Magnetic measurements were performed in the temperature range 1.72-400 K in external magnetic fields of up to 5 T, using a Quantum Design MPMS-5 SQUID magnetometer.

Results

The La$_{1-x}$Y$_x$Cu$_2$In system

According to the results of the X-ray phase analysis of the samples, unlimited solubility of yttrium in the LaCu$_2$In compound was observed. This leads to the formation of a continuous solid solution in the La$_{1-x}$Y$_x$Cu$_2$In system. The samples with an yttrium concentration lower than 5 % were single phase. However upon further increase of the yttrium content, an additional cubic phase with MgCu$_4$Sn-type structure appeared, in equilibrium with the MnCu$_2$Al-type phase. The amount of the secondary phase proportionally grew with increasing yttrium concentration, while the unit cell parameters of the Heusler phase decreased. For the Laves phase, for which a relatively broad homogeneity range has been reported, YCu$_{4.64-4.0}$In$_{0.36-1.0}$, no significant change of the unit cell was observed, the unit cell parameter being in good agreement with the value reported for the In-rich boundary (Table 1, Fig. 2).

The La$_{1-x}$Ce$_x$Cu$_2$In system

Physical properties of alloys belonging to the La$_{1-x}$Ce$_x$Cu$_2$In solid solution have been studied [7]; however, no systematic investigation has so far been carried out.

According to the results of the phase analysis of the samples of the La$_{1-x}$Ce$_x$Cu$_2$In system, the substitution of cerium for lanthanum at 870 K results in the formation of a continuous solid solution in the whole concentration range. The solution is based on the two ternary cubic Heusler phases, and all the samples were single-phase. The unit cell parameters decrease with increasing cerium concentration (Table 1, Fig. 3). It may be noted that a MgCu$_4$Sn–type phase is not known, neither in the Ce–Cu–In nor in the La–Cu–In system.

The La$_{1-x}$Gd$_x$Cu$_2$In system

The existence of a continuous solid solution with MnCu$_2$Al structure was observed at 870 K in the La$_{1-x}$Gd$_x$Cu$_2$In system. The solid solution is formed due to substitution of gadolinium atoms for lanthanum atoms in the original structure. An additional phase with MgCu$_4$Sn-type structure appeared in equilibrium with the Heusler phase, when the gadolinium content was in the range 12.5-5 at.%. However, the secondary phase was only present in small amounts (up to 10 wt.%). The unit cell parameters of the alloys of the La$_{1-x}$Gd$_x$Cu$_2$In system decrease with increasing gadolinium concentration (Table 1, Fig. 4). The presence of a second, Cu-rich phase in the quaternary and in the ternary boundary system, questions the exact composition of the Heusler phase on the Gd-rich side, and a certain Cu-deficiency cannot be excluded. It may be noted that GdCuIn (ideal stoichiometry of a half-Heusler phase) crystallizes with a ZrNiAl-type structure.

The Y$_{1-x}$Gd$_x$Cu$_2$In system

According to the results of the analysis of the X-ray diffraction patterns of the samples of the Y$_{1-x}$Gd$_x$Cu$_2$In system at 870 K, complete substitution of gadolinium

Table 1 Unit cell parameters of the solid solutions observed in the $RE_{1-x}RE'_x$Cu$_2$In (RE = Y, La, Ce, Gd) systems.

| Structure type (space group)	Cell parameters	Nominal composition of the sample
	La$_{1-x}$Y$_x$Cu$_2$In	
MnCu$_2$Al (*Fm-3m*)	a = 0.6854(1)-0.6608(3) nm V = 0.3220(2)-0.2885(1) nm^3	x = 0-1
	La$_{1-x}$Ce$_x$Cu$_2$In	
MnCu$_2$Al (*Fm-3m*)	a = 0.6854(1)-0.6796(1) nm V = 0.3220(2)-0.3138(1) nm^3	x = 0-1
	La$_{1-x}$Gd$_x$Cu$_2$In	
MnCu$_2$Al (*Fm-3m*)	a = 0.6854(1)-0.6653(1) nm V = 0.3220(2)-0.2945(1) nm^3	x = 0-1
MgCu$_4$Sn (*F-43m*)	a = 0.7255(1)-0.7243(3) nm V = 0.3819(1)-0.3799(2) nm^3	x = 0.5-1
	Y$_{1-x}$Gd$_x$Cu$_2$In	
MnCu$_2$Al (*Fm-3m*)	a = 0.6608(3)-0.6653(1) nm V = 0.2885(1)-0.2945(1) nm^3	x = 0-1
MgCu$_4$Sn (*F-43m*)	a = 0.7191(1)-0.7243(3) nm V = 0.3719(1)-0.3799(3) nm^3	x = 0-1
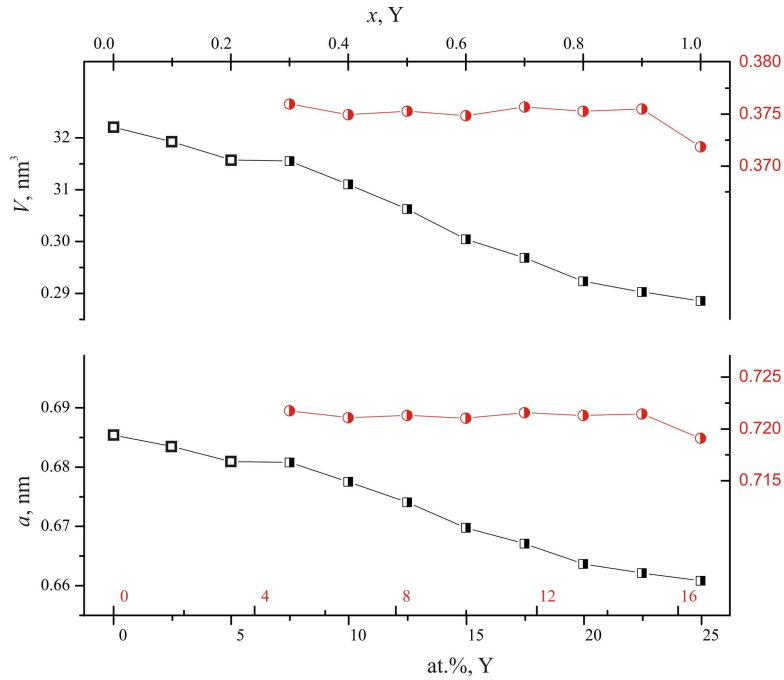
Fig. 2 Unit cell parameters of the phases with MnCu$_2$Al-type structure (squares) and MgCu$_4$Sn-type structure (circles) observed in the La$_{1-x}$Y$_x$Cu$_2$In system, as a function of the yttrium content.
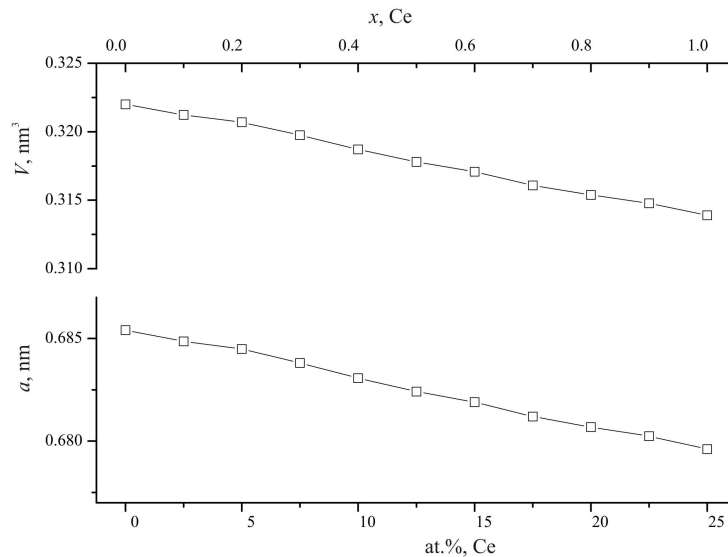

Fig. 3 Unit cell parameters of the La$_{1-x}$Ce$_x$Cu$_2$In phase with MnCu$_2$Al-type structure, as a function of the cerium content.

for yttrium takes place. In the whole concentration range, a phase with MgCu$_4$Sn-type structure (content lower than 15 wt.%) was also observed, in equilibrium with the dominant phase. The unit cell parameters of both phases slightly increase when yttrium is diluted with gadolinium. Such a behavior is in good agreement with the atomic radii of the rare-earth metals [12] (Table 1, Fig. 5).

Magnetic properties of the La$_{1-x}$Gd$_x$Cu$_2$In (x = 0.1-0.4) solid solution

The results of magnetic measurements performed on four selected La$_{1-x}$Gd$_x$Cu$_2$In alloys within the x = 0.1-0.4 concentration range, where no secondary phase was observed, are shown in Fig. 6. From this figure it is clearly seen that a gradual replacement of
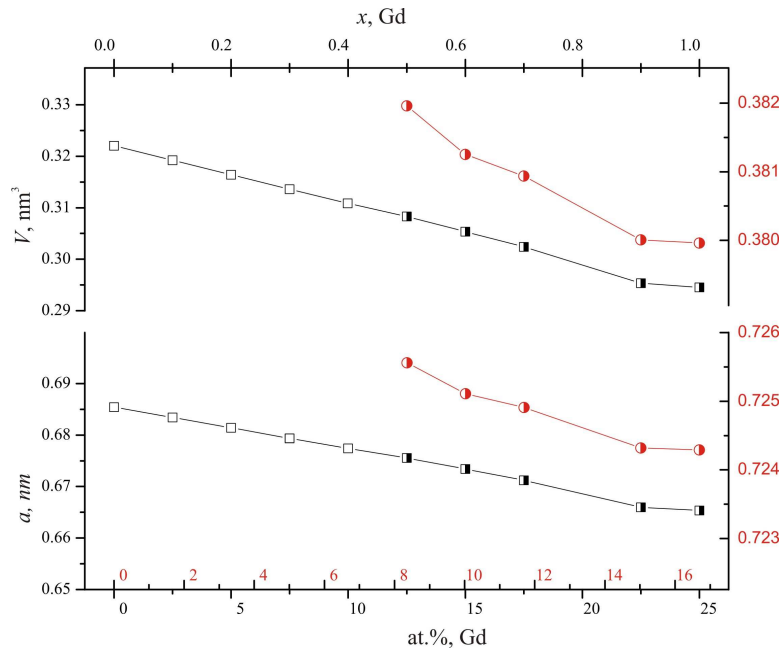
Fig. 4 Unit cell parameters of the phases with MnCu$_2$Al-type structure (squares) and MgCu$_4$Sn-type structure (circles) observed in the La$_{1-x}$Gd$_x$Cu$_2$In system, as a function of the gadolinium content.
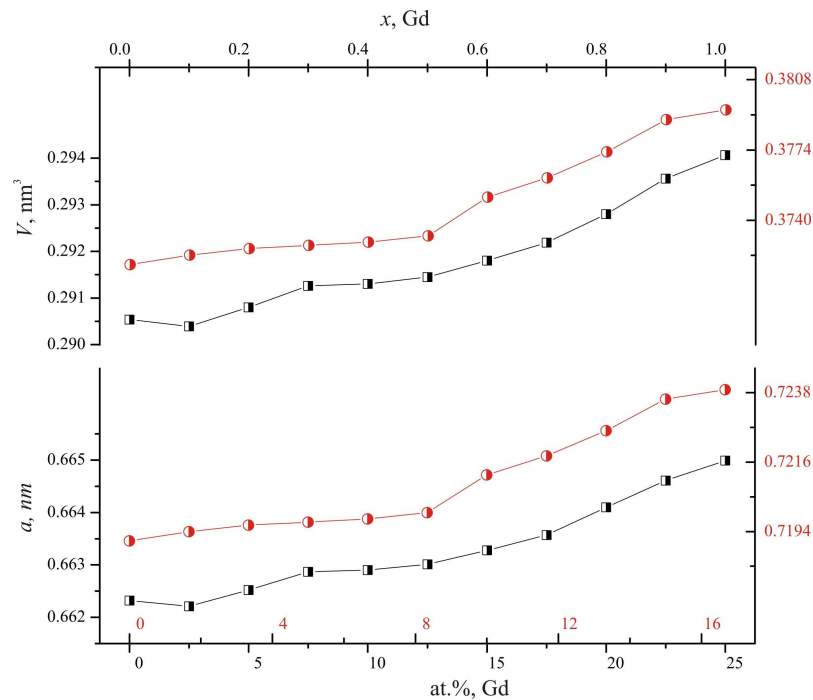

Fig. 5 Unit cell parameters of the phases with MnCu$_2$Al-type structure (squares) and MgCu$_4$Sn-type structure (circles) observed in the Y$_{1-x}$Gd$_x$Cu$_2$In system, as a function of the gadolinium content.

non-magnetic La^{3+} ions by magnetic Gd^{3+} ions significantly enhances the magnetic properties. This observation is true even for the La$_{0.9}$Gd$_{0.1}$Cu$_2$In sample, which has the lowest concentration of gadolinium (2.5 at.%). The inverse magnetic susceptibility (χ^{-1}) of the four representatives of the La$_{1-x}$Gd$_x$Cu$_2$In system, changes with temperature in a manner characteristic of Curie-Weiss paramagnets. This behavior contrasts with the temperature-independent Pauli paramagnetism observed for the pure LaCu$_2$In compound [3]. It is worth adding that the room temperature values of the molar susceptibility, normalized to 1 mole Gd atoms, of the four investigated samples differ little, which proves

the correct estimation of the gadolinium concentration. The values of the effective magnetic moment (μ_{eff}) and the paramagnetic Curie temperature (θ_p), obtained from least-quares fits of the Curie-Weiss function $\chi = C / (T - \theta_p)$ to the experimental data above 10 K, are summarized in Table 2. The values of μ_{eff} are close to the Russell-Saunders value of 7.94 μ_B for Gd^{+3} ions, which confirms the that the gadolinium ions are subjected to no significant influence of the crystal field ($L = 0$). The negative values of θ_p indicate dominating antiferromagnetic interactions, which increase with increasing gadolinium concentration. Such behavior should be expected when progressing in composition toward the GdCu$_2$In compound,

which is a strong antiferromagnet [8]. However, the magnetic susceptibility at low temperature (see upper inset to Fig. 6) shows no sign of an antiferromagnetic phase transition within the concentration range $x = 0.1$-0.4.

The magnetization curves obtained at 1.72 K (presented in the lower inset to Fig. 6) corroborate the paramagnetic state for all the investigated samples of the La$_{1-x}$Gd$_x$Cu$_2$In system. The magnetization measured in the highest field of 5 T, grows with increasing Gd content (x), but remains far from saturation. This is probably due to the large magnetic moment of the Gd^{3+} ion ($S = 7/2$), which requires higher magnetic fields to reach saturation.
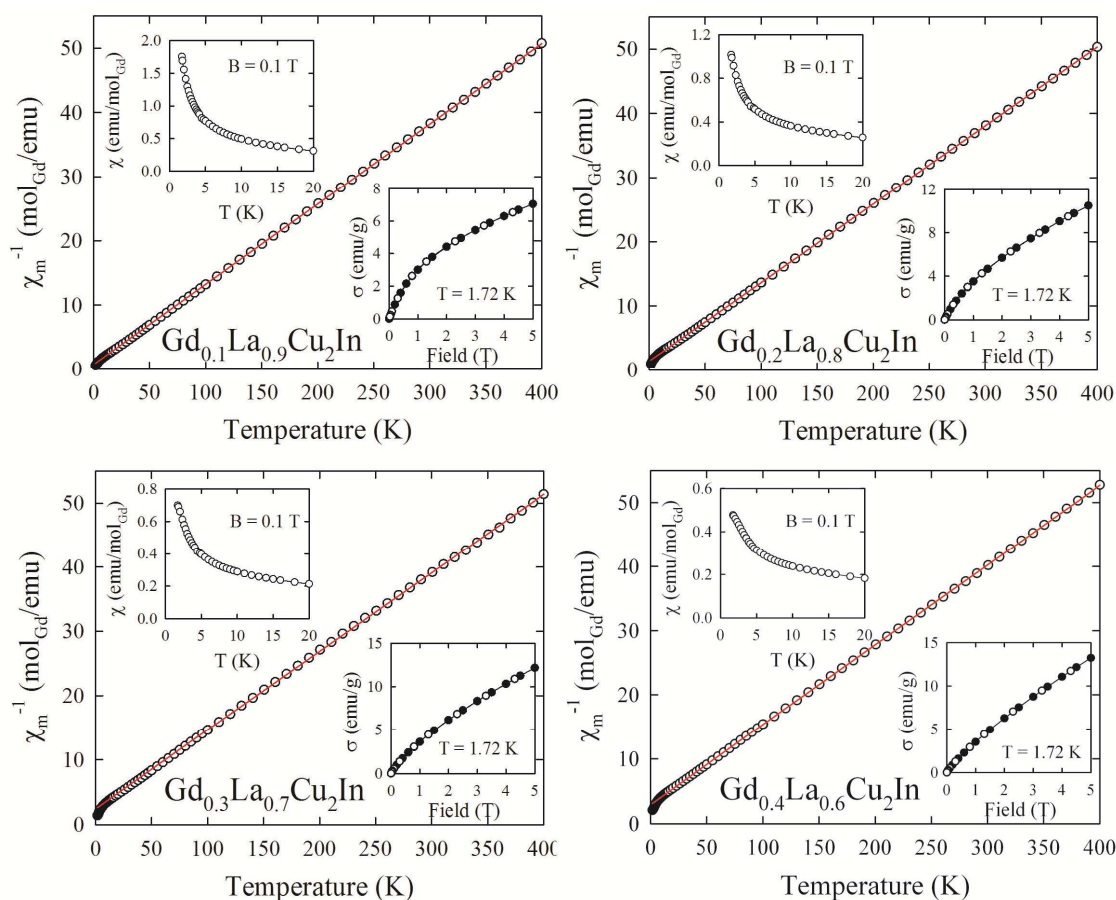

Fig. 6 Temperature dependence of the inverse magnetic susceptibility of the single-phase samples of the La$_{1-x}$Gd$_x$Cu$_2$In system, measured in a magnetic field of 0.1 T. The upper insets present the low-temperature susceptibility. The lower insets show the field dependence of the magnetization at $T = 1.72$ K, measured on increasing (full circles) and decreasing (open circles) the magnetic field.

Table 2 Effective magnetic moment (μ_{eff}) and paramagnetic Curie temperature (θ_p) for samples of the La$_{1-x}$Gd$_x$Cu$_2$In series, obtained from a least-squares fit to the Curie-Weiss law.

Composition	μ_{eff} [μ_B/Gd]	θ_p [K]
La$_{0.9}$Gd$_{0.1}$Cu$_2$In	7.99	-5.2
La$_{0.8}$Gd$_{0.2}$Cu$_2$In	8.07	-10.9
La$_{0.7}$Gd$_{0.3}$Cu$_2$In	8.18	-19.9
La$_{0.6}$Gd$_{0.4}$Cu$_2$In	8.03	-23.6

Discussion

Our assumptions concerning the possible formation of substitutional solid solutions in $RE_{1-x}RE'_xCu_2In$ systems were confirmed by the results of the phase analysis of the quasi-binary systems $La_{1-x}Y_xCu_2In$, $La_{1-x}Ce_xCu_2In$, $La_{1-x}Gd_xCu_2In$, and $Y_{1-x}Gd_xCu_2In$ in the full concentration range at 870 K. Replacement of lanthanum by yttrium, cerium or gadolinium, as well as yttrium by gadolinium, leads to the formation of continuous solid solutions based on the parent ternary compounds with $MnCu_2In$-type structure. The composition dependence of the unit cell parameters of these solid solutions is consistent with the size of the rare-earth metals [12]. In the case of replacement of lanthanum atoms by yttrium, cerium or gadolinium atoms, which are smaller in size, the unit cell parameter and the cell volume are consequently reduced (see Figs. 2-4). On the contrary, the cell parameters slightly increase (see Fig. 5) when the yttrium atoms are replaced by larger gadolinium atoms. It has been shown that the nature of the interactions between the components has a significant influence on the phase composition in the ternary systems RE–Cu–In (RE = Y, La, Ce, Gd) [13-16]. According to [13,16], YCu_4In and $GdCu_4In$, with $MgCu_4Sn$-type structure, are in equilibrium with YCu_2In and $GdCu_2In$, respectively, in the Cu-rich regions of the phase diagrams at 870 K. Laves phases commonly show high thermodynamic stability and it cannot be excluded that equilibrium had not yet been reached in the investigated alloys. Meanwhile, compounds with $MgCu_4Sn$-type structure do not form in the RE–Cu–In (RE = La, Ce) systems [14,15], and the samples of the $La_{1-x}Ce_xCu_2In$ system were all single phase.

Comparing the results obtained here with studies of the solubility of aluminum in $RECu_2In$ (RE = Y, La, Gd) [10], some significant differences can be noticed. The chemical nature and the atomic radius greatly affect the solubility of the fourth component in the $RECu_2In$ compound. The similar chemical affinity of the different rare-earth metals, their comparable size, and the isotypism of the $RECu_2In$ (RE = Y, La, Ce, Gd) compounds, favor the formation of continuous solid solutions with $MnCu_2Al$-type structure. On the contrary, replacement of indium by another p-element (aluminum) leads to the formation of limited solid solutions. The main reason for the limited solubility is the absence of isotypic $RECu_2Al$ (RE = Y, La, Gd)

compounds, and differences in the atomic radii and chemical properties of indium and aluminum.

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