Structural study of the pseudobinary Y(Ni,Cu)₂ system

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Abstract

The pseudobinary $Y(Ni_{1-x}Cu_x)_2$ compounds have been investigated by X-ray and neutron diffraction, density measurements as well as with electron probe microanalysis. The goal was to understand the mechanism behind the structural change from the cubic structure of $Y_{0.95}Ni_2$ (a cubic superstructure of the cubic Laves phase with ordered vacancies on the Y site) into the orthorhombic $CeCu_2$ type structure of YCu_2. 20% of Cu can be substituted for Ni in $Y_{0.95}Ni_2$ accompanied by an increase of the number of Y vacancies in the cubic superstructure. On the Cu-rich side a solid solution was found from YCu_2 to $Y(Ni_{0.5}Cu_{0.5})_2$. The substitution for Ni in the orthorhombic structure mainly causes a decrease of the lattice parameter a, giving rise to a 3.5% contraction of the unit cell volume. These two solid solutions are separated by a two-phase region. The thermal expansion among the cubic compounds hardly changes with the Cu concentration, whereas it increases in the orthorhombic range towards YCu_2.
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Keywords: A. Laves phases, rare-earth intermetallics; B. Crystal chemistry of intermetallics

1. Introduction

It has been known for a long time that YNi_2 and YCu_2 show different crystal structures, namely the $MgCu_2$ type structure (cubic Laves phase) and the orthorhombic $CeCu_2$ type structure [1], respectively. Recently it has been shown that YNi_2 crystallizes in a superstructure of the cubic Laves phase with the nominal composition $Y_{0.95}Ni_2$. This superstructure with the space group $F\bar{4}3m$ is characterized by ordered Y vacancies on the 4a sites and a doubling of the Laves phase unit cell parameter ($a' = 2a = 14.35$ Å) [2]. The structural data of YCu_2 are: orthorhombic $CeCu_2$ type structure (space group $Imma$, $a = 4.301$ Å, $b = 6.874$ Å and $c = 7.297$ Å at room temperature). These two structure types are not related. The $MgCu_2$ type structure is characterized by a diamond-like Y-sublattice surrounded by a tetrahedal Ni network, whereas the $CeCu_2$ type structure is a distorted modification of the hexagonal AlB_2 type structure, which is composed of alternating Ce and Cu planes along the orthorhombic b

direction (corresponding to the hexagonal axis of the undistorted AlB_2 type). Since Cu follows Ni in the periodic table the question may arise, why there is a change of the crystal structure within the family of this 1:2 compound, taking into account the fact that all the RFe_2, RCo_2 and part of the RMn_2 compounds show the cubic Laves phase structure. Recent theoretical investigations have shown that the stability of the $CeCu_2$ structure in YCu_2 is mainly caused by electronic band structure effects [3].

The goal of the present study was to gain additional experimental information concerning the mechanism behind this structural change. For this purpose a detailed investigation of the structural properties of the pseudobinary $Y(Ni_{1-x}Cu_x)_2$ system has been performed. In order to determine the solubility range and to search for the existence of an unknown ternary compound existing at a certain concentration, which might be the missing link between the cubic and orthorhombic structures, we have prepared several pseudobinary compositions of the $Y(Ni,Cu)_2$ series. The samples were studied by X-ray and neutron diffraction, electron probe microanalysis and density measurements with respect to their structural properties. Since the thermal expansion is intimately related to the structural stability,

measurements of the thermal expansion were performed for some concentrations.

2. Experimental

The intermetallic compounds have been prepared by induction-melting of the pure elements (Y 99.9%, Ni 99.99% and Cu 99.99%) in a water-cooled copper crucible. Part of the as-cast samples were wrapped in tantalum foils, sealed in evacuated silica tube and annealed at several temperatures between 923 and 1123 K for periods ranging between 2 and 3 weeks. The homogeneity and the composition of the samples were then analyzed by optical microscopy and electron probe microanalysis (EPMA) with a SX100 Cameca apparatus at 20 keV using YK_α, CuK_α and NiK_α lines.

X-ray diffraction (XRD) measurements at room temperature were performed on a Bruker D8 diffractometer, with CuK_α radiation. Temperature-dependent XRD measurements were done from 10 to 300 K with a Siemens D500 diffractometer equipped with a He flow cryostat from Oxford Instruments, using $Co\ K_\alpha$ radiation. Ge powder was used as an internal standard for correcting the instrumental errors.

The neutron diffraction (ND) experiments were performed on three samples at 300 K, using the PSD diffractometer 3T2 located in the Orphée reactor of the Léon Brillouin Laboratory. The wavelength was 1.225 Å and the neutron diffraction patterns were registered from 6 to 126° with steps of 0.05°. About 8 g of each sample were crushed, sieved below 100 μm and transferred under air into vanadium tubes.

All the X-ray and neutron diffraction patterns were refined using the Rietveld method with the FULLPROF code [4]. A multipattern analysis was performed to refine the X-ray and neutron diffraction patterns simultaneously.

The experimental densities were measured using an Accupyc 1330 pycnometer from Micromeritics.

3. Experimental results

3.1. X-ray diffraction at 300 K and microprobe analysis

Several $Y(Ni_{1-x}Cu_x)_2$ samples with $0 \leqslant x \leqslant 1$ were prepared in order to determine the homogeneity range and structural properties around the 1:2 composition within the ternary Y–Ni–Cu phase diagram. The samples were examined as-cast and after two to three weeks annealing treatment at 923, 1023 or 1073 K under a vacuum of 10^{-6} mbar. The results obtained by EPMA and XRD on the samples annealed at 1023 K are reported in Table 1. In order to obtain single-phase samples, it was necessary to vary the starting

Y/(Ni + Cu) ratio around 1:2. Owing to the Y vacancies, an excess of (Ni, Cu) had to be used for the cubic Ni-rich samples (see Table 1), whereas an excess of 4 at.% of Y is necessary for the Cu-rich samples. The foreign phases present in the $YNi_{0.5}Cu_{1.5}$, $YNi_{0.9}Cu_{0.95}$, $YNiCu$ and $YNi_{1.9}Cu_{0.2}$ sample material could not be detected in the XRD patterns, only in EPMA which detects precipitates of few micrometers. In the pseudobinary sample material studied with a varying 1:2 ratio, compounds with composition $Y(Ni_{1-y}Cu_y)_3$ and $Y(Ni_{1-y}Cu_y)_4$ with $y > 0.5$ were identified. A closer investigation of the ternary Y–Ni–Cu phase diagram is necessary in order to confirm the existence of these phases.

The analysis of these data around the 1:2 composition shows that the orthorhombic $CeCu_2$ type structure exists from YCu_2 up to $YNi_{0.9}Cu_{1.05}$ where almost 50% of Cu atoms are substituted by Ni. The variation of the orthorhombic lattice parameters with increasing Ni content shows mainly a decrease of the lattice parameter a ($\Delta a/a = -2.9\%$), whereas the decrease of b ($\Delta b/b = -0.5\%$) and c ($\Delta c/c = -0.1\%$) is much smaller (Fig. 1). The unit cell volume decrease $\Delta V/V$ is about 3.5%. The cubic superstructure of the Y–Ni boundary phase is maintained up to $YNi_{1.8}Cu_{0.4}$ and is accompanied by a 0.13% increase of the cell parameter and thus a 0.39% increase of the cell volume (Fig. 1). A sample prepared with the $YNi_{1.5}Cu_{0.5}$ starting composition decomposes into a mixture of a cubic phase $YNi_{1.83}Cu_{0.38}$ and an orthorhombic phase $YNi_{0.9}Cu_{1.07}$. This means that between the two single-phase regions a two-phase region exists, constituted by a mixture of the cubic and orthorhombic phases (Table 1). These investigations reveal no hint for the appearance of a new ternary phase distinct from the cubic one on the Ni-rich side or from the orthorhombic one on the Cu-rich side.

3.2. Density measurements

The densities of the single-phase samples (without inclusions indicated by a * in Table 1) have been measured at 300 K, in order to compare the calculated with the experimental densities (Table 2). The densities were calculated using the composition and the cell parameters reported in Table 1. For the Ni-rich compounds we have also calculated the densities assuming that there are no Y vacancies.

For the orthorhombic compounds, there is good agreement between the measured and calculated densities, with a (Ni + Cu)/Y ratio close to 2. Concerning the cubic compounds it is obvious that the deviation from the 1:2 stoichiometry is intimately related to Y vacancies. If we consider stoichiometric 1:2 samples or an excess of transition elements, the calculated densities are significantly larger than the measured densities.

Table 1
Data analysis of different $Y(Ni_{1-x}Cu_x)_2$ concentrations studied among the sample material annealed two weeks at 1023 K. The first column depicts the nominal concentration whereas the second column shows the actual concentration obtained from the microprobe analysis (the concentrations with * correspond to the compositions of the inclusions present in the matrix). The next columns give the lattice parameters (where they could be measured) and the cell volume obtained by refining the X-ray diffraction patterns at room temperature

| Starting compound	Microprobe analysis	Structure type	Lattice parameters			
			a (Å)	b (Å)	c (Å)	V (Å³)
$YCu_{1.92}$	YCu_2	$CeCu_2$	4.301(1)	6.874(1)	7.297(1)	215.7
$YNi_{0.29}Cu_{1.63}$	$YNi_{0.30(1)}Cu_{1.70(1)}$	$CeCu_2$	4.261(1)	6.858(1)	7.291(1)	213.1
$YNi_{0.5}Cu_{1.5}$	$YNi_{0.50(1)}Cu_{1.51(1)}$	$CeCu_2$	4.229(1)	6.859(1)	7.300(1)	211.6
	$YNi_{1.04}Cu_{2.9}$ *					
$YNi_{0.48}Cu_{1.44}$	$YNi_{0.49(1)}Cu_{1.51(1)}$	$CeCu_2$	4.231(1)	6.858(1)	7.302(1)	211.6
$YNi_{0.67}Cu_{1.25}$	$YNi_{0.69(1)}Cu_{1.29(1)}$	$CeCu_2$	4.199(1)	6.850(1)	7.299(1)	209.9
$YNi_{0.9}Cu_{1.05}$	$YNi_{0.90(1)}Cu_{1.08(1)}$	$CeCu_2$	4.176(1)	6.848(1)	7.289(1)	208.4
$YNi_{0.9}Cu_{0.95}$	$YNi_{0.93(2)}Cu_{1.06(2)}$	$CeCu_2$	4.174(1)	6.847(1)	7.288(1)	208.3
	$YNi_{0.83}Cu_{0.2}$ *					
YNiCu	$YNi_{0.93(1)}Cu_{1.06(1)}$	$CeCu_2$	4.179(1)	6.848(1)	7.293(1)	208.7
	$YNi_{2.1(4)}Cu_{1.09(4)}$ *					
$YNi_{1.5}Cu_{0.5}$	$YNi_{0.90(1)}Cu_{1.07(1)}$	$CeCu_2$	4.177(1)	6.850(1)	7.284(1)	208.4
	$YNi_{1.83(2)}Cu_{0.38(2)}$	Cubic	14.375(2)			2970
$YNi_{1.8}Cu_{0.4}$	$YNi_{1.86(5)}Cu_{0.41(1)}$	Cubic	14.369(2)			2967
$YNi_{1.9}Cu_{0.2}$						
	$YNi_{1.94(5)}Cu_{0.22(2)}$					
	$YNi_{0.9}Cu_{0.09}$ *	Cubic	14.368(2)			2966
$Y_{0.95}Ni_2$	$Y_{0.95}Ni_2$	Cubic	14.357(2)			2959
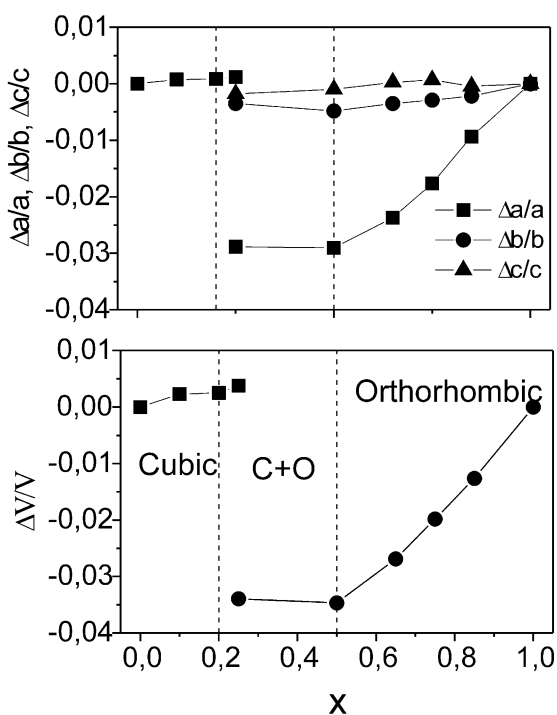
Fig. 1. Concentration dependence of the normalized lattice parameters ($\Delta a/a$, $\Delta b/b$, $\Delta c/c$) and normalized cell volume ($\Delta V/V$) relative to those of the binary compounds for the $Y(Ni_{1-x}Cu_x)_2$ pseudobinary system.

3.3. Neutron diffraction experiments

The X-ray scattering factors of Ni and Cu are close and therefore do not allow us to distinguish the two elements in the XRD patterns. We have performed neutron diffraction (ND) measurements on three selected compounds $YNi_{0.5}Cu_{1.5}$, $YNi_{0.9}Cu_{1.05}$ and $YNi_{1.8}Cu_{0.4}$ in order to check whether there are solid solutions or ordered substitutions of Ni and Cu in both homogeneity ranges.

The ND patterns of $YNi_{0.9}Cu_{1.05}$ and $YNi_{0.5}Cu_{1.5}$ can be very well refined in the $CeCu_2$ type structure with a statistical distribution of the Ni and Cu atoms (Tables 3 and 4 and Fig. 2). No superstructure lines are found and no sign of a lowering of the crystal symmetry is detectable. A preferential site occupation of Ni atoms in YCu_2 would change the symmetry since there is only one equivalent site for all the Cu atoms in the $CeCu_2$ type structure. The refinement of the occupation numbers leads to YNiCu and $YNi_{0.5}Cu_{1.5}$ which are close to the compositions found in the EPMA experiments. The refined z_Y, y_{Cu} and z_{Cu} atomic positions remain close to those of YCu_2 ($z_Y = 0.544(2)$, $y_{Cu} = 0.050(2)$ and $z_{Cu} = 0.162(2)$). The calculated interatomic distances (Table 5) decrease progressively as the Ni content increases, which is in agreement with the smaller metallic radius of Ni compared to that of Cu.

The ND pattern of $YNi_{1.8}Cu_{0.4}$ was refined starting from the structure of $Y_{0.95}Ni_2$ assuming a random substitution of Ni by Cu. Because of the large number of atomic sites in the superstructure of the cubic Laves phase (5 Y and 4 Ni/Cu) the XRD and ND patterns were refined simultaneously, using the multipattern option of FULLPROF [4]. In $Y_{0.95}Ni_2$, vacancies were only found on the Y 4a site. Both microprobe and density measurements on $YNi_{1.8}Cu_{0.4}$ indicate 10% of Y vacancies which is twice as large as in the transitional

Table 2
Experimental and calculated densities for selected $Y(Ni,Cu)_2$ compounds. The nominal composition corresponds to the first column of Table 1, whereas the calculated is derived from the EPMA analysis and is used to calculate the density. For the cubic Ni rich compounds, the densities were calculated assuming (a) Y vacancies or (b) no Y vacancies

Nominal composition	Composition used for d_{calc}	$d_{exp.}$ (g/cm³)	$d_{calc.}$ (g/cm³)
$YNi_{0.29}Cu_{1.63}$	$YNi_{0.3}Cu_{1.7}$	6.65(1)	6.65
$YNi_{0.5}Cu_{1.5}$	$YNi_{0.5}Cu_{1.5}$	6.69(1)	6.71
$YNi_{0.67}Cu_{1.25}$	$YNi_{0.7}Cu_{1.3}$	6.69(1)	6.69
$YNi_{0.9}Cu_{1.05}$	$YNi_{0.90}Cu_{1.08}$	6.73(1)	6.73
$YNi_{1.8}Cu_{0.4}$	$Y_{0.9}Ni_{1.62}Cu_{0.36}$ (a)	7.16(1)	7.165
	$YNi_{1.8}Cu_{0.4}$ (b)		7.881
$YNi_{1.9}Cu_{0.2}$	$Y_{0.93}Ni_{1.77}Cu_{0.19}$ (a)	7.08(1)	7.203
	$YNi_{1.9}Cu_{0.2}$ (b)		7.638
$Y_{0.95}Ni_2$	$Y_{0.95}Ni_2$ (a)	7.29(1)	7.26
	YNi_2 (b)		7.41

Table 3
Results of the Rietveld refinement of the neutron diffraction pattern of $YNi_{0.9}Cu_{1.05}$. The fractional position parameters are denoted by x, y, z. B is the isotropic temperature factor and N is the relative occupation number. U, V, W denote the half width parameters

Atom		x	y	z	B	N
Y	4e	0	0.25	0.5444 (1)	0.89 (3)	1
Ni	8h	0	0.0523 (1)	0.1630 (2)	1.08	0.502
Cu						0.498
a (Å):	4.1769	b (Å):	6.8486	c (Å):	7.2885	
V (Å³):	208.5					
U:	0.333	V:	−0.498	W:	0.248	
R_{profil}	9.62%	R_{Bragg}	5.14%			

Table 4
Results of the Rietveld refinement of the neutron diffraction pattern of $YNi_{0.5}Cu_{1.5}$. The fractional position parameters are denoted by x, y, z. B is the isotropic temperature factor and N is the relative occupation number. U, V, W denote the half width parameters

Atom		x	y	z	B	N
Y	4e	0	0.25	0.5454 (1)	0.90 (3)	1
Ni	8h	0	0.0522(1)	0.1644 (2)	1.04	0.26
Cu						0.75
a (Å):	4.229	b (Å):	6.857	c (Å):	7.301	
U:	0.335	V:	−0.498	W:	0.248	
V (Å³):	211.7					
R_{profil}	9.03%	R_{Bragg}	4.6%			

compound $Y_{0.95}Ni_2$ (5%). Therefore all the Y occupancy factors have been refined. The results of the refinements are reported in Table 6 and shown in Fig. 3. The Ni/Cu ratio was fixed to the value obtained by EPMA (0.22). The total amount of Y vacancies (8.7%) is close to the EPMA and density measurements (10%). The Y vacancies are mainly located on the Y1 (4a) site, but also on the Y4 site and weakly on the Y3 and Y5 sites. Comparing the interatomic distances with those in
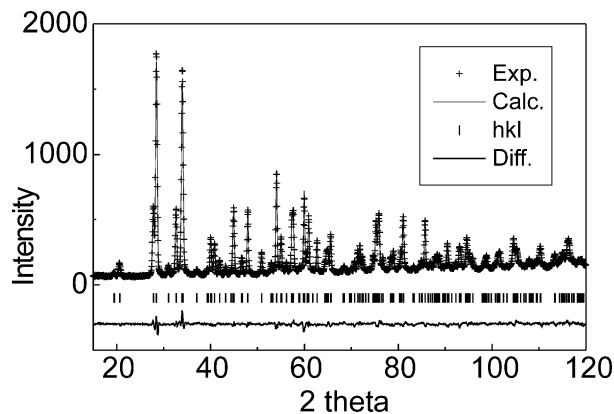

Fig. 2. Experimental and refined neutron diffraction pattern of $YNi_{0.90}Cu_{1.05}$.

Table 5
Comparison of the interatomic distances (Å) in orthorhombic $Y(Ni_{1−x}Cu_x)_2$ compounds. $d1$, $d2$ and $d3$ are shown in Fig. 5

Distance	YCu_2	$YNi_{0.5}Cu_{1.5}$	YNiCu
d_{M-M} ($d1$)	2.462	2.505	2.482
d_{M-M} ($d2$)	2.505	2.456	2.443
d_{M-M} ($d3$)	2.750	2.713	2.708
d_{M-Y}	2.964	2.942	2.912
	2.974	2.963	2.972
	3.101	3.085	3.065
	3.111	3.095	3.092
d_{Y-Y}	3.498	3.492	3.485
	3.692	3.660	3.654

Table 6
Results of the Rietveld refinement of the neutron diffraction pattern of $YNi_{1.8}Cu_{0.4}$. The fractional position parameters are denoted by x, y, z. B is the isotropic temperature factor and N is the relative occupation number. U, V, W denote the half width parameters

Atom	Site	x	y	z	B	N
Y1	4a	0	0	0	1.19 (4)	0.452
Y2	4b	0.5	0.5	0.5		1
Y3	24g	0.0057	0.25	0.25		0.980
Y4	16e	0.1012	0.1012	0.1012		0.832
Y5	16e	0.6257	0.6257	0.6257		0.985
Ni1	16e	0.3117	0.3117	0.3117	0.65(1)	0.815
Cu1	16e					0.185
Ni2	16e	0.8122	0.8122	0.8122		0.815
Cu2	16e					0.185
Ni3	48h	0.0653	0.0653	0.8077		0.815
Cu3	48h					0.185
Ni4	48h	0.0623	0.0623	0.3120		0.815
Cu4	48h					0.185
Y vacancies						8.7%
a (Å):	14.372(1)					
V (Å³):	2968					
U:	0.427	V:	−0.498	W:	0.2475	
R_{profil}	11.4%	R_{Bragg}	5.38%			

$Y_{0.95}Ni_2$ (see Table 7) shows that the Cu-for-Ni substitution leads rather to a rearrangement than to an increase of the interatomic distances.
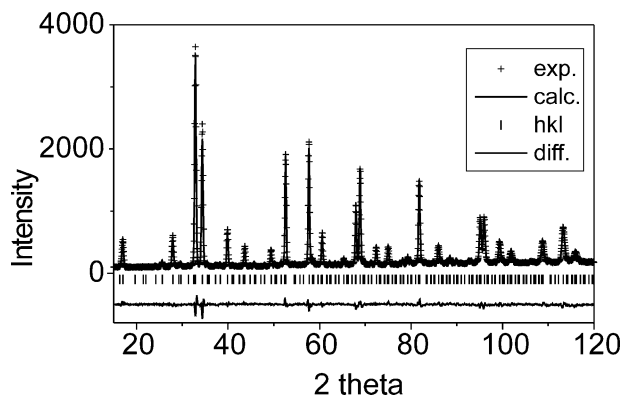
Fig. 3. Experimental and refined neutron diffraction pattern of $YNi_{1.8}Cu_{0.4}$.

Table 7
Comparison of the interatomic distances in $Y_{0.95}Ni_2$ and in the boundary compound of the cubic region

Distance	$Y_{0.95}Ni_2$	$YNi_{1.8}Cu_{0.4}$
d_{M2-M3}	2.4176	2.4889
d_{M1-M1}	2.4718	2.5076
d_{M3-M4}	2.5376	2.5280
d_{M1-M4}	2.5512	2.5589
d_{M4-M4}	2.5733	2.5275
d_{M2-M2}	2.6017	2.5323
d_{Y4-M3}	2.7881	2.7759
d_{Y5-M3}	2.8419	2.8895
d_{Y3-M1}	2.8531	2.9088
d_{Y5-M2}	2.9176	2.9625
d_{Y3-M4}	2.9300	2.9595
d_{Y3-M3}	2.9612	2.9623
d_{Y2-M4}	2.9721	2.9689
d_{Y5-M4}	3.0187	2.9847
d_{Y1-M3}	3.0948	3.0656
d_{Y3-M2}	3.0962	3.0540
d_{Y4-M4}	3.1497	3.1474
d_{Y4-M1}	3.5255	3.0548
d_{Y1-Y4}	2.4855	2.5194
d_{Y3-Y5}	3.1695	3.1538
d_{Y2-Y5}	3.1815	3.1295
d_{Y3-Y4}	3.3073	3.3211

3.4. Thermal expansion measurements

The thermal expansion was studied by XRD. The thermal variation of the cell volume of $Y_{0.95}Ni_2$, $YNi_{1.8}Cu_{0.4}$, $YNi_{0.9}Cu_{1.05}$ and YCu_2 is shown in Fig. 4a. Surprisingly the two cubic phases and $YNi_{0.90}Cu_{1.05}$ display a similar relative volume expansion. A fit of a Debye function to the thermal expansion of these three compounds leads to an average Debye temperature of 262 ± 15 K. The thermal expansion of YCu_2 is larger, with a smaller Debye temperature (197 ± 9 K). The thermal expansion of the orthorhombic cell parameters is anisotropic, with $\Delta a/a < \Delta c/c < \Delta b/b$ (Fig. 4b). The Ni substitution considerably lowers the $\Delta b/b$ and $\Delta c/c$ thermal expansion, whereas $\Delta a/a$ remains almost
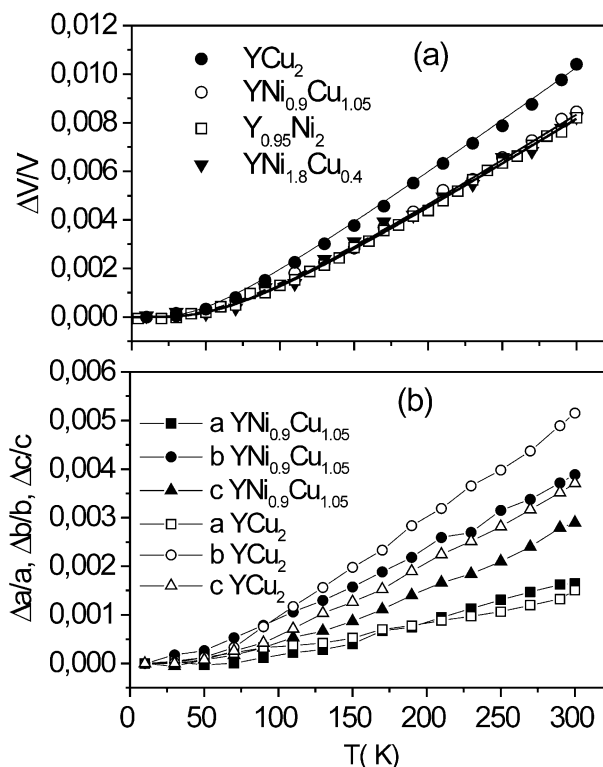

Fig. 4. (a) Normalized unit cell volume of the cubic $Y_{0.95}Ni_2$ and $YNi_{1.8}Cu_{0.4}$ compounds in comparison with the orthorhombic $YNi_{0.9}Cu_{1.05}$ and YCu_2 compounds. The lines through the data points are obtained by a fit of the Debye function. (b) Normalized lattice parameters a, b, c of the orthorhombic YCu_2 and $YNi_{0.9}Cu_{1.05}$. The temperature variation in b and c directions is much more influenced by the Ni substitution as compared to the a direction. The lines through the data points are just a guide for the eyes.

unchanged. This means that the Ni substitution lowers the anisotropy of the thermal expansion.

4. Discussion

The study of the pseudobinary $Y(Ni_{1-x}Cu_x)_2$ system annealed at 1023 K has shown that about 20% of Ni can be substituted by Cu while preserving the cubic superstructure of $Y_{0.95}Ni_2$ whereas 50% of Cu can be replaced by Ni in the orthorhombic YCu_2. A comparable solubility limit has been reported for the Cu-rich side of the isostructural $Gd(Cu_{1-x}Ni_x)_2$ [5]. The ND analysis has shown that in both homogeneity ranges there is a random distribution of Cu and Ni atoms. These two domains are separated by a two-phase range. No intermediate ternary phase ("missing link") with a different structure than the cubic $MgCu_2$ type or the orthorhombic $CeCu_2$ type structure has been observed.

The Ni for Cu substitution in the orthorhombic phase affects mainly the a parameter, whereas the b and c parameters are only weakly decreasing. A closer inspection of the interatomic distances in the transition metal (M) sublattice reveals an interesting behavior. The three

M–M distances (M = Ni, Cu), shown in Fig. 5 are related to the cell parameters and atomic positions according to the following formulas:

$$d1 = \sqrt{4\left(y_M^2 b^2 + z_M^2 c^2\right)} \quad (1)$$

$$d2 = \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{1}{2} - 2z_M\right)^2 c^2} \quad (2)$$

$$d3 = \left(\frac{1}{2} - 2y_M\right)b \quad (3)$$

As can be seen from these formulas, the shortest distance ($d1$) has its main component along the c axis, the second one ($d2$) along the a axis, whereas the third one ($d3$) is proportional to b. As can be seen from Table 5 there is an anomalous variation of the shortest distance $d1$ when substituting the smaller Ni atoms for Cu in YCu$_2$. First, the distance increases from 2.462 Å in YCu$_2$ to 2.505 Å in YNi$_{0.5}$Cu$_{1.5}$, then on further Ni substitution it decreases again to 2.482 Å in YNiCu. This shows that there is a highly anisotropic shifting of the atoms due to the substitution.

The thermal variation of the lattice parameters of the orthorhombic compounds shows an almost opposite behavior compared to the above-discussed variation as a function of the concentration x in the pseudobinary series, i.e, the smallest thermal variation is observed for a and the largest for b. The large thermal expansion in b direction is plausible, because the compressibility is also largest in this direction [3,6]. A further confirmation of the outstanding behavior in the b direction has been obtained from a study of the lattice dynamics in YCu$_2$ [7].
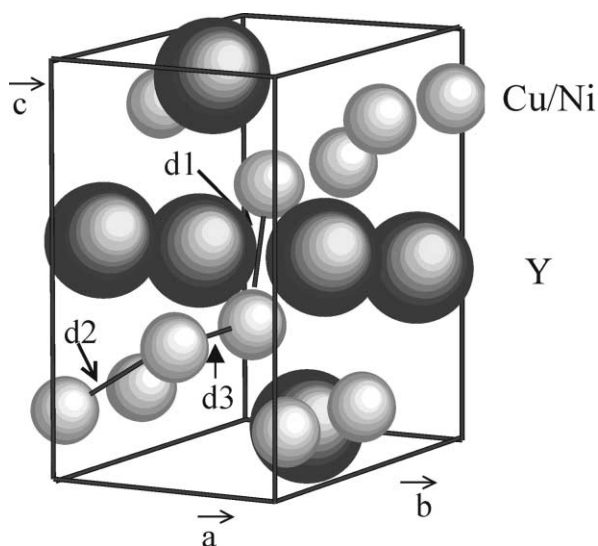

Fig. 5. The arrangement of the Y and Cu/Ni atoms in the orthorhombic CeCu$_2$ type structure: $d1$, $d2$ and $d3$ denote the nearest Cu/Ni–Cu/Ni distances.

On the cubic (Ni-rich) side of the pseudobinary series only 20% of Ni can be substituted by Cu. Interestingly, this hardly affects the cubic lattice parameter a (see Fig. 1), since the effect of the Cu substitution is compensated by an increasing amount of Y vacancies. Theoretical investigations have shown that the formation of vacancies on the Y sites is essential for the stability of the cubic phase in the case of YNi$_2$ [8], which is the last member of the YM$_2$ family (with M = Mn, Fe, Co, Ni) showing the cubic structure. The vacancies on the Y sites allow for a relaxation of stresses, caused by the deviation of the radius ratio r_Y/r_{Ni} from the ideal value 1.225 for the cubic Laves phase (the Ni atoms are too small in case of YNi$_2$) [8]. Considering only space-filling arguments, one would have expected that due to the larger radius of Cu, the MgCu$_2$ structure without vacancies should be stabilized upon Cu for Ni substitution, but the opposite effect (i.e., an increasing number of vacancies) is observed. This leads to the conclusion that band structure effects are crucial for the change of the structure upon Cu substitution. This is confirmed by electronic band structure calculations [3] showing that due to band structure effects, YCu$_2$ cannot be stabilized in the MgCu$_2$ structure under ambient conditions.

Ab initio total energy calculations performed for Y$_{0.95}$Ni$_2$, YNi$_2$ and YCu$_2$ [3,8] allowed calculation of the total energy and the enthalpy of formation in the experimentally observed and in the other possible structures. The difference in the enthalpies of formation between the CeCu$_2$ and MgCu$_2$ structures for YCu$_2$ is ≈ -0.12 eV/atom, whereas it is only ≈ 0.02 eV/atom for YNi$_2$. Taking into account the Y vacancies in Y$_{0.95}$Ni$_2$ this difference is only slightly increased (≈ 0.03 eV/atom). This means that in YCu$_2$ the stability of the CeCu$_2$ structure relative to the MgCu$_2$ structure (or to the cubic superstructure) is about four times larger than the stability of the MgCu$_2$ superstructure relative to the CeCu$_2$ structure in Y$_{0.95}$Ni$_2$. This may explain why a larger amount of Ni can be substituted in YCu$_2$ than Cu in Y$_{0.95}$Ni$_2$ without changing the structure.

5. Conclusion

The study of the pseudobinary Y(Ni$_{1-x}$Cu$_x$)$_2$ compounds showed that 20% of Ni can be substituted by Cu in Y$_{0.95}$Ni$_2$ and 50% of Cu can be substituted by Ni in YCu$_2$. These two solid solution ranges are separated by a two phase domain. No intermediate ternary phase has been observed. The structural study has shown that the Cu for Ni substitution in Y$_{0.95}$Ni$_2$ leads to an increase of Y vacancies, located on several Y sites. The size reduction due to Y vacancies compensates the expected increase of the volume due to the Cu substitution, and the lattice parameter increases

only weakly with the Cu content. The Ni for Cu substitution in YCu_2 leads to a strong reduction of the orthorhombic lattice parameter a. In contrast, the thermal variation of a is the smallest among the three lattice parameters for all the studied orthorhombic compounds.

Acknowledgements

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