Crystal Structure of Nonstoichiometric Copper-Substituted La(Ni$_{1-z}$Cu$_z$)$_x$ Compounds Studied by Neutron and Synchrotron Anomalous Powder Diffraction

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The structural properties of the potential battery electrode materials LaNi$_4$Cu, LaNi$_{4.4}$Cu, LaNi$_5$Cu, and LaNi$_{4.5}$Cu$_{1.5}$ have been investigated by neutron and anomalous synchrotron powder diffraction. The nonstoichiometry of such AB_x (5 ≤ x ≤ 6) compounds has been described in a structure derived from the hexagonal CaCu$_5$-type structure by replacement of the A atoms by dumbbells of B atoms. In these copper-substituted compounds, Cu can occupy any of the four available nickel sites. From a joint refinement procedure using both neutron and synchrotron data, the copper-to-nickel ratio at each B site has been determined. This shows that substitution is not random and that copper occupies some crystallographic sites preferentially. The results are discussed and compared to other substituted AB_5 systems. © 1999 Academic Press

INTRODUCTION

AB_5-type hydride-forming compounds have attracted serious commercial interest in the last few years because of their widespread application in rechargeable nickel metal hydride (NiMH) batteries. The breakthrough of this new battery type was accomplished by the discovery that the electrochemical long-term cycling stability of the parent compound LaNi$_5$ could be substantially improved by replacing part of the B-type atoms (Ni) by other transition metals (such as Mn or Co) within the AB_5 stoichiometry. This resulted in multicomponent compounds (1).

Recently, it has been shown that both the alloy cost and the electrochemical cycling stability can be improved by employing so-called nonstoichiometric compounds (2, 3). These AB_x compounds ($x > 5$), which contain an excess of B-type elements, can be described within the hexagonal CaCu$_5$-type structure by replacing part of the A-type atoms by dumbbells of B-type atoms oriented along the **c** axis. It has been observed that Cu plays an important role in the

stability of these compounds. From previous work on the La(Ni$_{1-z}$Cu$_z$)$_x$ system, it was suggested from cell parameter variations measured using X-ray powder diffraction data (XRD) that the dumbbells probably consist of nickel atoms only, while the Cu atoms occupy a sixfold position around these dumbbells (4). However, the absence of contrast between copper and nickel when studied by XRD does not allow one to fully solve the structures. Attempts to refine the structures from neutron diffraction (ND) data (5) lead to rather unreliable results related to instability of the refinements.

Recently, the site occupancies in the compound LaNi$_{3.55}$Mn$_{0.4}$Al$_{0.3}$Co$_{0.75}$ were successfully investigated using multiwavelength synchrotron powder diffraction (6). We therefore used both the resolution and the contrast enhancement provided by anomalous synchrotron powder diffraction in combination with the neutron diffraction data to fully determine the structure of the nonstoichiometric Cu-containing compounds, especially in terms of the copper-to-nickel substitution ratios at the different available sites.

EXPERIMENTAL METHODS

Sample Preparation and Characterization

The samples were prepared as described in Ref. 4. Stoichiometry and homogeneity were controlled by XRD, metallographic examination, and electron probe microanalysis (EPMA). Density measurements were performed with an Accupyc 1330 apparatus.

Diffraction Experiments

ND measurements were performed on the high-resolution two-axis diffractometer D2B at the Institut Laue–Langevin in Grenoble. The wavelength was set to 1.593 Å. About 10 g of sample with a grain size less than 36 μm

contained in a sealed silica tube under vacuum was placed in the neutron beam. The patterns were recorded over the range 15°–162° in 2θ by steps of 0.05°. The Fermi lengths (b_i) used for the refinement are given in Table 1.

The synchrotron diffraction patterns have been collected at the Powder Diffraction Beam Line BM16 at the ESRF (7). Because of their high absorption coefficient ($\mu \approx 1710$ cm^{-1} at 8318 eV) the samples were prepared in a flat-plate geometry. The sample holders were filled with a dried paste made of 95 wt% of powdered sample (< 36 μm) and 5 wt% of polytetrafluoroethylene (PTFE). This preparation gives excellent flatness of the surface, a good grain orientation, and perfect cohesion of the powder under the ω rotation and φ spinning during the data collection. PTFE, which acts as a binder, contains light elements and gives only one line in the diffraction pattern at $d = 4.894$ Å, out of the range of interest of the studied samples. The wavelength used ($\lambda = 1.4905$ Å) corresponds to an energy $E = 8318$ eV, 14 eV below the K edge of the free atom ($E_{Ni} = 8332$ eV). The exact value of the energy was determined by the refinement of the wavelength with a silicon standard. The efficiency of the nine detectors was checked with a corundum sample. The real (f') and imaginary (f'') components of the anomalous coefficients for each element were calculated using the method of Cromer and Libermann (8, 9). The f' values for the different elements are given in Table 1.

Refinement Procedure

In the hexagonal CaCu$_5$-type structure, the Ca atoms lie on the $1a$ position at the origin and the Cu atoms are located on the $2c$ and $3g$ sites in the basal and middle planes, respectively ($P6/mmm$ space group). It has already been shown (10) that in nonstoichiometric AB_x compounds, part of the A atoms in the Wyckoff position $1a$ are replaced by dumbbells of B-type atoms occupying the site $2e$ and oriented along the **c** axis. Such a possibility has been described in detail in Ref. (4). In that case, the B atoms forming

a hexagon in the $z = 0$ plane around the dumbbell are no longer on a $2c$ site but shrink into the $6l$ position. With this assumption, all the crystallographic sites are partially occupied with an occupancy factor τ_i, except the $3g$ site, which is considered to be unaffected and fully occupied ($\tau_2 = 3$). Thus, the general formula AB_x can be written as $A_{1-y}B_{5+2y}$, where the parameter y is defined from x by

$$y = \frac{(x-5)}{(x+2)}. \qquad [1]$$

Each parameter τ_i can be deduced from the y value shown in Table 2 and according to the following description:

$$A_{1-y}^{1a}B_{2-6y}^{2c}B_3^{3g}B_{6y}^{6l}B_{2y}^{2e}. \qquad [2]$$

If we now consider a substituted compound $A(B_{1-z}B'_z)_x$, four atomic ratio parameters ξ_i that represent the ratio of B' atoms replacing the B atoms must be taken into account. The system leads therefore to four unknown parameters. It is, however, possible to reduce the problem to three parameters if one considers the following equation relying on the total number of atoms B':

$$\left(\sum B'\right) \sum_{i=1}^{4} \tau_i \cdot \zeta_i = z \cdot (5 + 2y). \qquad [3]$$

Three different cases have been studied:
- LaNi$_{5.4}$

The presence of dumbbells was first checked for the non-substituted nonstoichiometric compound LaNi$_{5.4}$, for which all parameters $\zeta_i = 0$. Neutron and synchrotron powder diffraction data were treated simultaneously using joint refinement. Occupancy factors of the crystallographic sites were set in such a way that each time a dumbbell was present, the $1a$ site was empty and the atoms in the $2c$ site are displaced in the $6l$ site. With these constraints, only one

TABLE 1
Experimental Conditions for the Different Recorded Patterns

Source	Instrument	λ (Å) [E] (eV)	$\Delta E = E - E_{K_{Ni}}$ (eV)	Z (e$^-$) or	b (fm)	f' (e$^-$)	2θ range (°)	Step (°)
Synchrotron (ESRF)	BM 16 (K_{Ni} edge)	1.4905 [8318]	−14	$Z_{Ni} = 28$ $Z_{Cu} = 29$ $Z_{La} = 57$		$f'_{Ni} = -6.099$ $f'_{Cu} = -2.330$ $f'_{La} = -1.436$	12–134	0.02
Neutron (ILL)	D2B	1.5932	—		$b_{Ni} = 10.3$ $b_{Cu} = 7.72$ $b_{La} = 8.27$		15–162	0.05

Note. $E_{K_{Ni}}$ is the edge position for the free atom of nickel, f' is the real part of the anomalous coefficient calculated with the method of Cromer and Liberman (8, 9), and b is the Fermi length.

TABLE 2
Description of the Different Crystallographic Sites in Non-Stoichiometric $A_{1-y}(B_{1-z}B'_z)_{5+2y}$ Compounds

Wyckoff position	Atoms	Occupancy	τ_i	ζ_i
1a	A	$\tau_0 A$	$\tau_0 = 1 - y$	—
2c	B, B'		$\tau_1 = 2 - 6y$	
3g	B, B'	$\tau_i(B(1 - \zeta_i) + B'\zeta_i)$	$\tau_2 = 3$	$0 \le \zeta_i \le 1$
6l	B, B'		$\tau_3 = 6y$	
2e	B, B'		$\tau_4 = 2y$	

Note. τ_i is the occupancy factor of each site and ζ_i represents the atomic ratio between B' and B atoms on each site.

parameter is necessary to fully describe the stoichiometry of this compound.

● LaNi$_4$Cu

For this stoichiometric sample, as no dumbbells are expected, the parameters τ_i are integers (1, 2, 3, 0, 0, respectively). The total amount of copper was determined by EPMA and the copper distribution between the sites 2c and 3g was refined with only one parameter using synchrotron data alone.

● LaNi$_{4.4}$Cu, LaNi$_5$Cu, and LaNi$_{4.5}$Cu$_{1.5}$

As the dumbbell model has been verified with the sample LaNi$_{5.4}$, the relations between the τ_i parameters and $y(x)$ (Eqs. [1] and [2]) have been used for these samples. To reduce the number of free parameters, the total amount of copper was also assumed to match the EPMA measured values (Eq. [3]). Therefore, the distribution of copper within the four B-type sites was reduced to three refined parameters.

The data treatment was carried out in a joint Rietveld refinement between neutron and synchrotron data with the program GSAS (11). For the Rietveld analysis the background was obtained by a linear interpolation between the peaks approximating the general shape of the background

combined with a fit by a cosine Fourier series having five refined parameters. For neutron data, the lineshape was described by a Thomson Cox Hastings pseudo-Voigt (TCHpV) function (12). For the synchrotron patterns, the super-Lorentzian line profiles were modeled by a superposition of two Lorentzian functions (TCHpV function with Gaussian part equal to zero) reproducing the narrow part at the top (shape 1) and the large wings at the bottom (shape 2) of the diffraction peaks. These two functions were introduced into the refinement using two phases which were fully correlated for their structural parameters but independent of their respective linewidths (parameters X and Y) and relative amounts. The starting values for the occupation number of each B and B' atom were calculated assuming a random distribution of copper on the Ni sites.

RESULTS

XRD, metallographic examination, and EPMA showed that all the intermetallic compounds were homogeneous and single-phase except for LaNi$_5$Cu, for which precipitation of about 2 wt% of the fcc (Ni, Cu) secondary phase was observed. Therefore, in the present work, this latter compound must be considered an $AB_{5.8}$ compound instead of an AB_6 one. All the diffraction patterns have been correctly indexed in the $hP6$ CaCu$_5$-type structure (space group $P6/mmm$), and the results for all samples are given in Table 3. The measured and calculated densities are also reported in this table. For LaNi$_5$Cu, the secondary phase (Ni, Cu) has been taken into account in the density calculation even if it represents a very small amount (2 wt%). Good agreement is observed (within 1% accuracy) between the densities measured by pycnometry and those obtained from cell parameters and EPMA.

Rietveld analysis for the nonstoichiometric copper-free sample LaNi$_{5.4}$ confirms the presence of Ni dumbbells replacing the La atoms in the crystallographic cell. The results of the joint refinement are given in Table 4. Good agreement is obtained between the stoichiometry calculated

TABLE 3
Characterization of the Studied Alloys by EPMA and X-Ray Diffraction

Compound	Microprobe analysis (EPMA)	Cell parameters			Density	
		a (Å)	c (Å)	V (Å^3)	$\rho_{\text{meas.}}$	$\rho_{\text{calc.}}$
LaNi$_{5.4}$	La$_{1.00(1)}$Ni$_{5.39(1)}$	4.9902(1)	3.9990(1)	86.23	8.24(1)	8.30(8)
LaNi$_4$Cu	La$_{1.00(1)}$Ni$_{4.02(2)}$Cu$_{0.99(1)}$	5.0379(1)	4.0064(1)	88.06	8.18(1)	8.25(5)
LaNi$_{4.4}$Cu	La$_{1.00(1)}$Ni$_{4.36(1)}$Cu$_{0.99(1)}$	5.0112(1)	4.0204(1)	87.45	8.30(2)	8.28(4)
LaNi$_5$Cu	La$_{1.00(1)}$Ni$_{4.84(1)}$Cu$_{0.95(2)}$	4.9861(1)	4.0324(1)	86.80	8.24(1)	8.31(11)
	+ Ni$_{79(1)}$Cu$_{21(1)}$(2 wt.%)	3.5455(1)				
LaNi$_{4.5}$Cu$_{1.5}$	La$_{1.00(1)}$Ni$_{4.50(1)}$Cu$_{1.49(1)}$	4.9864(1)	4.0481(1)	87.15	8.32(1)	8.31(9)

Note. The calculated densities are obtained from the stoichiometry as defined by Eqs. [1] and [2].

TABLE 4
Structural Data on LaNi$_{5.4}$: Atomic Coordinates (x, y, z), Displacement Factors (B), and Refined and Calculated Occupancy Factors (τ_i)

Site	x	y	z	B (Å^2)	τ_i refined	τ_i calculated
1a	0	0	0	0.86 (2)	0.942(1)	0.947
2c	$\frac{1}{3}$	$\frac{2}{3}$	0		1.654(6)	1.683
3g	$\frac{1}{2}$	0	$\frac{1}{2}$	0.91(2)	3.00 (fixed)	3.000
6l	0.281(1)	2x	0		0.348(6)	0.317
2e	0	0	0.312(2)		0.116(2)	0.106

	$R_{\omega p}$	R_p	R_{F1}	R_{F2}	χ^2	N_{ref}
ND	4.95	3.31	4.58	—	—	52
Synchrotron	15.22	12.43	5.74	11.55	—	57
Global	7.14	5.44	—	—	1.44	

30 variables $P6/mmm$ Cell parameters $a = 4.9902(1)$ Å   Refined: La$_{0.942}$Ni$_{5.116}$ = $AB_{5.43(2)}$
$c = 3.9990(1)$ Å

from the EPMA results and the refined ones. Therefore, the hypothesis of dumbbells replacing the La atoms was validated for the binary compound and was also adopted for the other nonstoichiometric compounds in the present work.

The structural data for LaNi$_4$Cu, LaNi$_{4.4}$Cu, LaNi$_5$Cu, and LaNi$_{4.5}$Cu$_{1.5}$ are given in Tables 5–8. For all compounds, convergence was reached and low global χ^2 values (less than 2.4) were obtained, indicating good quality of the refinement. For the synchrotron data, two agreement factors (R_{F1} and R_{F2}) corresponding, respectively, to the narrow and broad peak contributions are given. Representative

parts of the diffraction patterns are shown in Fig. 1 for LaNi$_{4.5}$Cu$_{1.5}$. The relative proportion ζ_i between nickel and copper has been obtained for each B site. For low x values ($x = 5.4$), the dumbbells and the 6l hexagons are formed with nickel only, whereas for larger x values ($x = 5.8$ and 6.0), these crystallographic positions begin to be significantly occupied by copper.

TABLE 6
Structural Data on LaNi$_{4.4}$Cu: Atomic Coordinates (x, y, z), Displacement Factors (B), Calculated Occupancy Factors (τ_i), and Refined Atomic Ratio (ζ_i)

Site		x	y	z	B (Å^2)	τ_i	ζ_i
1a	La	0	0	0	1.21(2)	0.952	
2c	Ni	1/3	2/3	0		1.714	0.70(1)
2c	Cu						0.30(1)
3g	Ni	1/2	0	1/2	1.26(2)	3.00	0.858(4)
3g	Cu						0.142(4)
6l	Ni	0.280(1)	2x	0		0.286	1.0(1)
6l	Cu						0.0(1)
2e	Ni	0	0	0.320(3)		0.095	1.0(1)
2e	Cu						0.0(1)

	$R_{\omega p}$	R_p	R_{F1}	R_{F2}	χ^2	N_{ref}
ND	5.11	3.34	4.03	—	—	55
Synchrotron	13.3	10.7	6.21	7.56	—	60
Global	8.21	5.85	—	—	2.06	

32 variables $P6/mmm$ Cell parameters $a = 5.0112(1)$ Å   La$_{0.952}$(Ni$_{4.15}$Cu$_{0.94}$)
$c = 4.0204(1)$ Å   = $A_{0.952}B_{5.095}$

TABLE 5
Structural Data on LaNi$_4$Cu: Atomic Coordinates (x, y, z), Displacement Factors (B), Calculated Occupancy Factors (χ_i), and Refined Atomic Ratio (ζ_i)

Site		x	y	z	B (Å^2)	τ_i	ζ_i
1a,	La	0	0	0	0.30(2)	1.00	
2c,	Ni	1/3	2/3	0		2.00	0.769(5)
2c	Cu						0.231(5)
3g	Ni	1/2	0	1/2	0.14(3)	3.00	0.821(3)
3g	Cu						0.179(3)

	$R_{\omega p}$	R_p	R_{F1}	R_{F2}	χ^2	N_{ref}
Synchrotron	12.35	9.84	5.08	5.10	1.74	60

15 variables $P6/mmm$ Cell parameters $a = 5.0379(1)$ Å   LaNi$_4$Cu
$c = 4.0064(1)$ Å

TABLE 7
Structural Data on LaNi$_5$Cu: Atomic Coordinates (x, y, z), Displacement Factors (B), Calculated Occupancy Factors (τ_i), and Refined Atomic Ratio (ζ_i)

Site		x	y	z	B (Å^2)	τ_i	ζ_i
1a	La	0	0	0	1.27(2)	0.899	
2c	Ni	1/3	2/3	0		1.394	0.72(4)
2c	Cu						0.28(4)
3g	Ni	1/2	0	1/2	1.25(2)	3.00	0.872(5)
3g	Cu						0.128(5)
6l	Ni	0.282(1)	2x	0		0.606	0.95(5)
6l	Cu						0.05(5)
2e	Ni	0	0	0.307(2)		0.202	0.71(6)
2e	Cu						0.29(6)

	$R_{\omega p}$	R_p	R_{F1}	R_{F2}	χ^2	N_{ref}
ND	5.10	3.49	4.30	—	—	60
Synchrotron	14.8	12.1	7.19	10.7	—	66
Global	8.86	6.45	—	—	2.39	

34 variables $P6/mmm$ Cell parameters a = 4.9861(1) Å   La$_{0.899}$(Ni$_{4.34}$Cu$_{0.86}$)
c = 4.0324(1) Å   = $A_{0.899}B_{5.202}$

$Fm3m$ a = 3.5455(1) Å   Ni$_{79}$Cu$_{21}$ (2 wt%)

DISCUSSION

According to the sample characterization (Table 3), it is possible to obtain nonstoichiometric $hP6$ CaCu$_5$-type AB_x samples with copper in the range $5 \leq x \leq 6$. As already shown in Ref. (4), the copper content (z) is an important parameter to take into account to control the stoichiometry. From the two expected AB_6 samples, only the LaNi$_{4.5}$Cu$_{1.5}$ ($z = 0.25$) is single-phase, whereas in the present study LaNi$_5$Cu ($z = 0.166$) is in fact an $AB_{5.8}$ compound with precipitation of the fcc (Ni, Cu) phase. Concerning the cell parameters (Fig. 2), we observed, on one hand, that the **c**-axis parameter increases with both **x** and **z**. On the other hand, the **a**-axis parameter decreases with the stoichiometry **x** but increases with the copper amount **z**. As a consequence, the cell volume, which mainly depends on the **a**-axis ($V = a^2c\sqrt{3}/2$), follows the same behavior as this latter parameter: it decreases with **x** and increases with **z** (Fig. 2c). This is in agreement with the fact that the larger radius of copper (1.28 Å) leads to an increase of both cell parameters whereas the presence of dumbbells induces an increase of the **c**-axis and a decrease of the **a** axis. It is worthwhile to note that the cell volume is an important parameter with regard to the potential application of these compounds. It is known that the logarithm of the equilibrium plateau pressure of the formed hydride decreases linearly with the cell volume of the metallic compounds (13).

Moreover, the discrete volume expansion observed during the hydrogenation process is dependent on the nonstoichiometry (14) and plays a very important role in the decrepitation process and, thus, in the cycle life of such materials.

In a former attempt to refine the copper-to-nickel ratio using neutron data alone, we obtained rather unreliable results, although the statistics of the data were good enough. This fact was attributed to a lack of contrast between nickel and copper. In addition, the number of intensity-dependent refined parameters (three occupancy factors ζ_i, two site positions (x_{6l}, z_{2e}), and two displacement factors (B_{La}, $B_{Ni,Cu}$)) was rather high compared to the number of independent reflections (around 50). Therefore, it was decided to couple neutron and synchrotron data to do the following:

(i) To take advantage of the contrast provided by the anomalous effect. If we compare the scattering factors at $\theta = 0$ for nickel [$Z_{Ni} + f'_{Ni}$] and copper [$Z_{Cu} + f'_{Cu}$] (Table 1), the contrast is not very different from what is obtained with neutrons. However, the scattering factor difference is negative with anomalous X-ray diffraction ($f_{Ni}(\theta) - f_{Cu}(\theta) < 0$), whereas it is positive with neutrons ($b_{Ni} - b_{Cu} > 0$). It must also be pointed out that the contrast obtained from the anomalous effect increases as a function of $\sin(\theta)/\lambda$, which is not the case for neutrons. Moreover, photons interact with electrons, whereas neutrons are scattered by nuclei, which means that the two techniques probe the same structural parameters through different particles.

TABLE 8
Structural Data on LaNi$_{4.5}$Cu$_{1.5}$: Atomic Doordinates (x, y, z), Displacement Factors (B), Calculated Occupancy Factors (τ_i), and Refined Atomic Ratio (ζ_i)

Site		x	y	z	B (Å^2)	τ_i	ζ_i
1a	La	0	0	0	0.88(2)	0.875	
2c	Ni	1/3	2/3	0		1.250	0.68(4)
2c	Cu						0.32(4)
3g	Ni	1/2	0	1/2	1.10(2)	3.00	0.782(4)
3g	Cu						0.218(4)
6l	Ni	0.286(3)	2x	0		0.750	0.83(4)
6l	Cu						0.17(4)
2e	Ni	0	0	0.311(1)		0.250	0.45(4)
2e	Cu						0.55(4)

	$R_{\omega p}$	R_p	R_{F1}	R_{F2}	χ^2	N_{ref}
ND	5.01	3.27	3.96	—	—	55
Synchrotron	12.3	10.3	6.04	8.98	—	62
Global	8.41	6.27	—	—	2.36	

32 variables $P6/mmm$ Cell parameters a = 4.9864(1) Å   La$_{0.875}$(Ni$_{3.93}$Cu$_{1.32}$)
c = 4.0481(1) Å   = $A_{0.875}B_{5.250}$

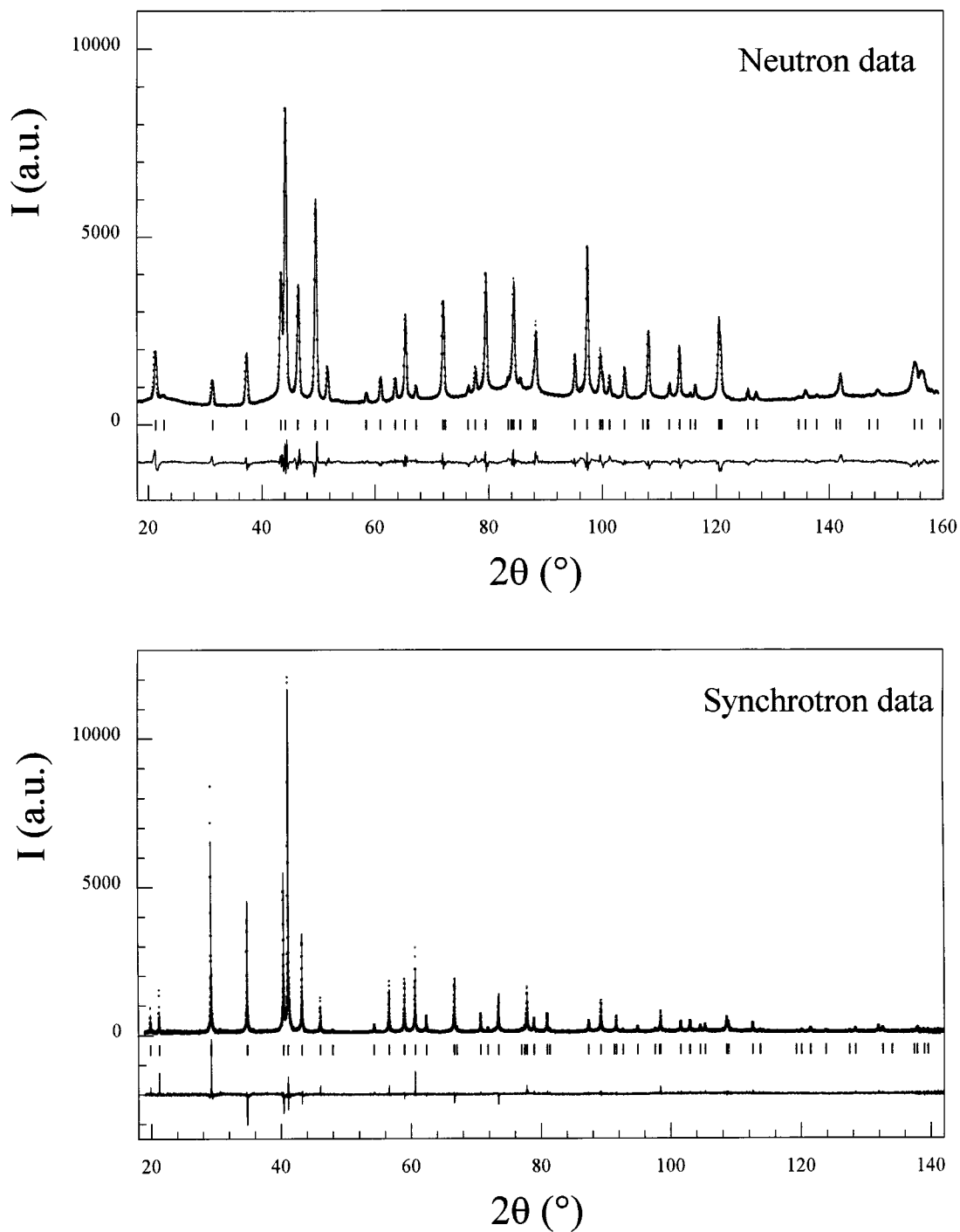**FIG. 1.** Refined diffraction patterns of LaNi$_{4.5}$Cu$_{1.5}$: neutron (top) and synchrotron (bottom) data. For each pattern, observed (dots), calculated (solid line), and difference curves (below) are shown. Vertical bars correspond to line positions.

(ii) To obtain twice the number of reflections (about 100) for the same number of intensity-dependent structural parameters (7) using joint refinement.

The values obtained for the global χ^2 (less than 2.4) testify to the quality of the refinements for all compounds. How-ever, if one compares the R factors for X-ray and neutron radiation, it can be observed that the R_p values obtained for synchrotron data are rather high. Since the R_F factors are relatively good, the structural model is unambiguous. This problem is therefore attributed to some incomplete
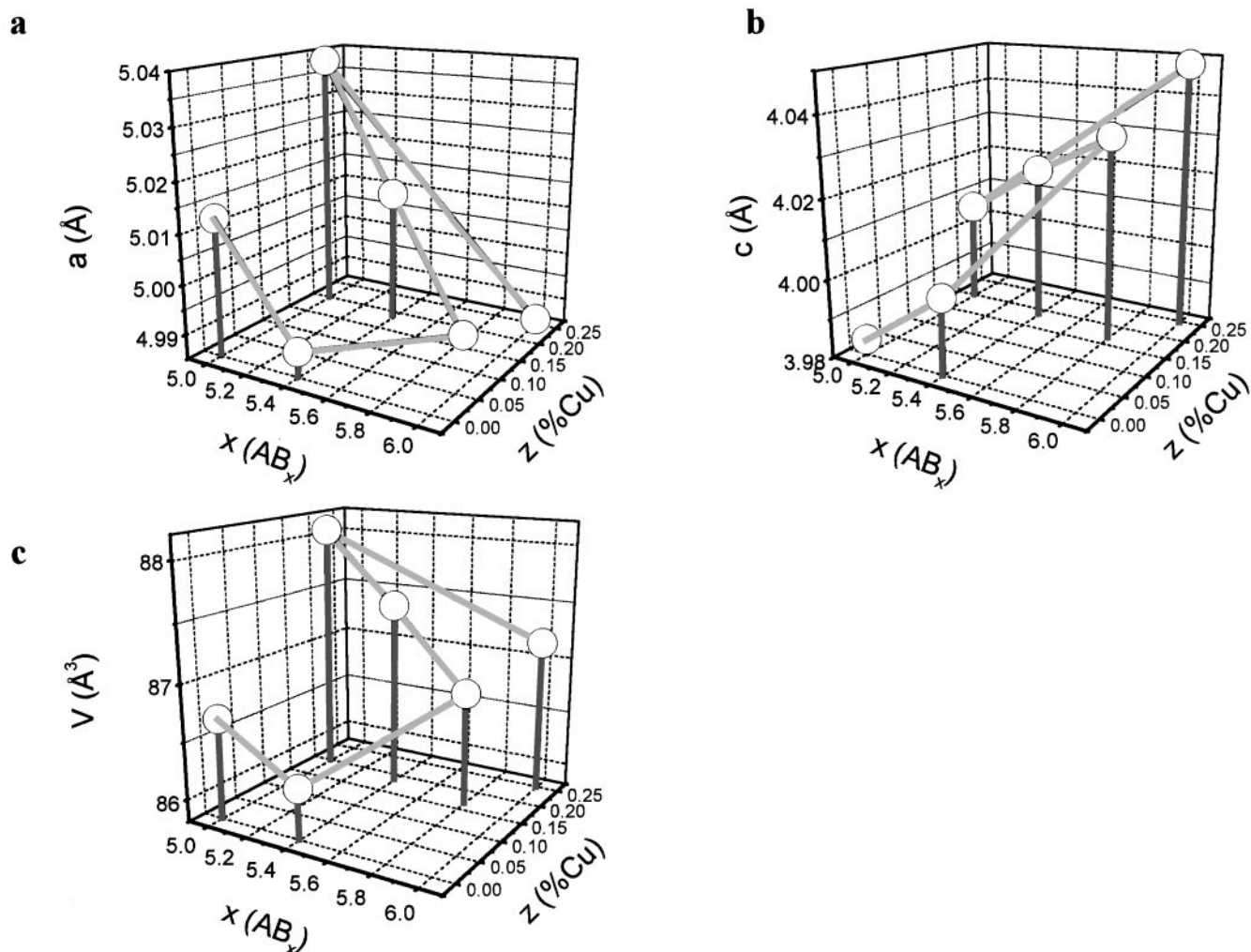
FIG. 2. Three-dimensional representation of the cell parameters (a and b) and volume (c) as a function of the stoichiometry **x** (AB_x) and of the copper content **z** (La(Ni$_{1-z}$Cu$_z$)$_x$). The line between data points is only a guide for the eyes. The data for LaNi$_5$ have been added to the plot for comparison (21).

corrections related to surface roughness and absorption effects in flat plate geometry. More probably, it is related to the difficulty in modeling the peak shapes of the synchrotron data. The super-Lorentzian character of the lineshape has already been observed in previous work (6) and was attributed to a nonhomogeneous distribution of grains having various degrees of crystallinity (15). The R_{F2} factors, attributed to the broad part at the bottom of the diffraction peaks, are systematically larger than those obtained for the narrow profile (R_{F1}). This is attributed not only to some correlation of this part of the peak shape with the background but also to some uncertainty in the deconvolution of F_{obs}. However, as the structural parameters are fully linked in the refinement for both profiles, this is not expected to affect the results significantly.

From the analysis of the Cu-free compound LaNi$_{5.4}$, the hypothesis of B-atom dumbbells replacing La atoms in the structure is confirmed. This is supported by the refined crystallographic data (Table 4) and also by the density measurements. Eventually, the z_{2e} coordinate of the $2e$ site ($z_{2e} = 0.312(2)$) allows one to calculate the distance between the two atoms forming a dumbbell, according to

$$d = 2z_{2e}c. \qquad [4]$$

For LaNi$_{5.4}$, this leads to 2.49(2) Å, which is in very good agreement with the distance calculated from the sum of two atomic radii of nickel (2.48 Å with $r_{Ni} = 1.24$ Å). The same arguments are also valid for the three Cu-containing compounds. However, because of the small radius difference between Ni and Cu and the estimated standard deviations (esd) of the z_{2e} coordinates, it was not possible to correlate this parameter with the copper-to-nickel ratio in this site.

Nevertheless, the refinement of occupancy factors has allowed us to determine the amount of copper on each site. The results are summarized in Tables 5–7 and in Fig. 3. On one hand, it shows that, for all compounds, the 2c site is systematically richer in copper compared to a random distribution. On the other hand, the 3g site is systematically depleted versus random distribution. For the stoichiometric compound LaNi$_4$Cu, our results can be compared to previous work reported by Achard *et al.* (16). From neutron diffraction data, they found a Cu atomic ratio of 0.27(2) for the 2c site and 0.15(1) for the 3g position. This is in rather good agreement with our synchrotron data and confirms the preference of copper for the 2c site. However, this is unexpected because generally in LaNi$_{5-s}$M$_s$ substituted (M = Mn, Fe, Al, Si) compounds (17), atoms larger than Ni

occupy the 3g position preferentially. These results must also be compared to those reported for LaNi$_4$Co (18). In that case, a preference for the 3g site is also observed for cobalt. It was attributed to atomic radius size effects (r_{Co} = 1.25 Å), but our present results show that because copper is larger than nickel (r_{Cu} = 1.28 Å), this size criterion is not the only parameter to take into account. The electronic configuration must also be considered. Photoemission measurements are actually in progress to investigate the band structures of this type of substituted alloy (19).

It also has to be noted that the displacement or so-called thermal factors (Bs) obtained for the LaNi$_4$Cu sample are lower than those for the other compounds in the present work. This can be attributed to the higher degree of order in this stoichiometric compound compared to that in the
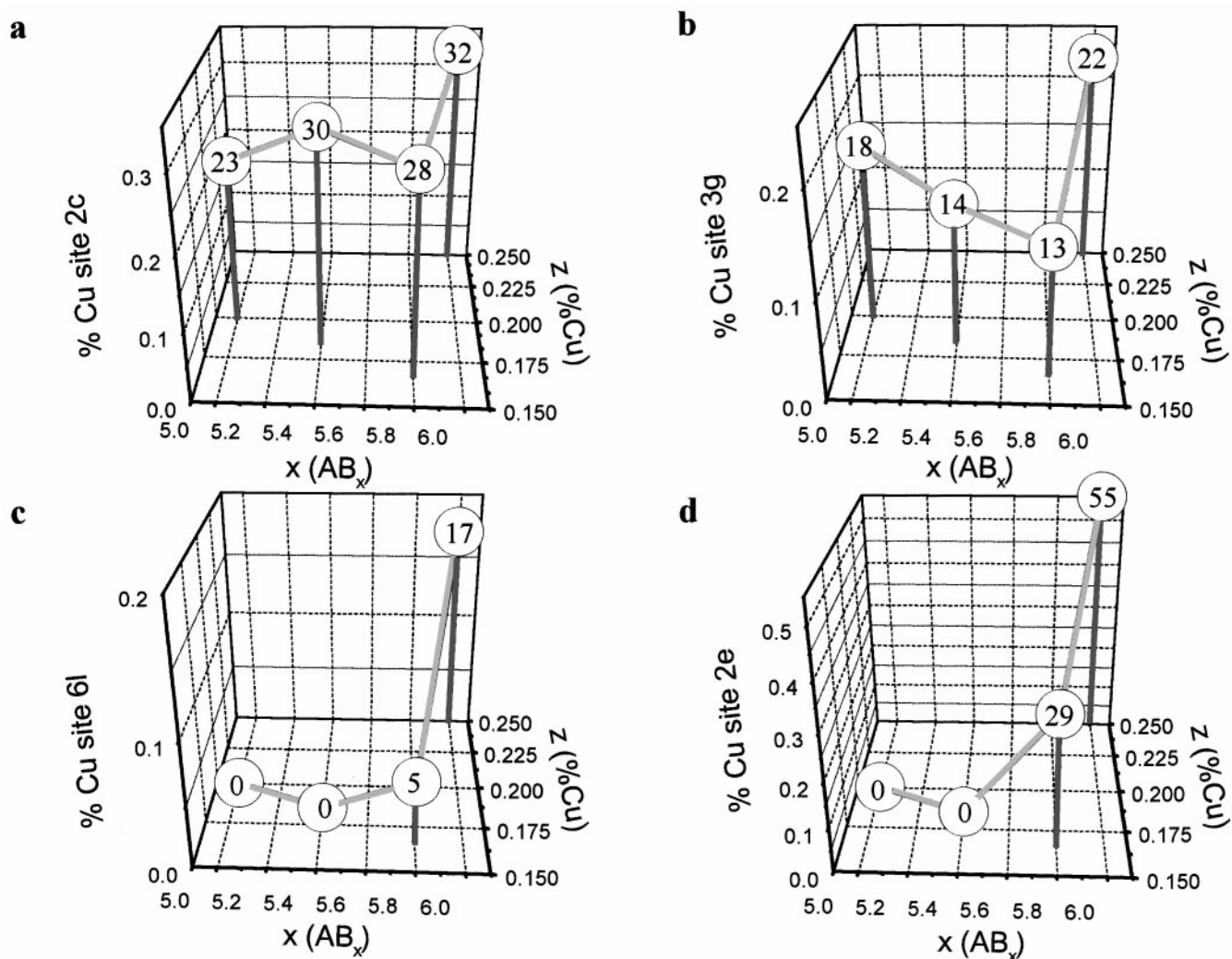

FIG. 3.   Three-dimensional distribution of copper atoms in sites 2c (a), 3g (b), 6l (c), and 2e (d) as a function of the stoichiometry **x** (AB$_x$) and the copper content **z** (La(Ni$_{1-z}$Cu$_z$)$_x$). The line between data points is only a guide for the eyes. Circled numbers indicate the amount of copper on each site in percentage points.

nonstoichiometric ones. However, our values must also be related to those of Ref. (16), which are also larger: $B_{1a} = 0.72(5)$; $B_{2c} = 0.74(5)$; $B_{3g} = 0.61(3)$. As a matter of fact, displacement parameters are very sensitive to the Q domain of the collected data. As the neutron diffraction peaks are significant even at high Q, they usually lead to more reliable values for these parameters than X-ray data. The observed differences for LaNi$_4$Cu parameters can be related to strong absorption effects when using synchrotron data. It demonstrates the interest of joint refinement of neutron and synchrotron data to overcome this problem.

For a low x value ($x = 5.4$) the $2e$ and $6l$ positions are made of nickel only, whereas for larger x values ($x = 5.8$ and 6.0), these crystallographic positions start to be occupied by copper (see Figs. 3c and 3d, respectively). For a low value of x, this is in fairly good agreement with the results of Notten et al. (4), which claim that the dumbbells are made of nickel atoms only. However, the assumption that the position $6l$ was made of pure copper is not confirmed by the present work.

These results can also be compared to the recent investigation of nonstoichiometric Mn-containing compounds, La$_{0.982}$(Ni$_{0.755}$Mn$_{0.245}$)$_{5.04}$ (which corresponds to $AB_{5.14}$ in the AB_x description) and La$_{0.925}$(Ni$_{0.834}$Mn$_{0.166}$)$_{5.15}$ (i.e., $AB_{5.5}$), where the Mn atomic ratios were measured by neutron diffraction (20). In these compounds, a clear preference of the manganese atoms for the $3g$ site is observed and the $2c$ site is almost pure nickel. The dumbbell site ($2e$) is found to be occupied by manganese only, whereas the $6l$ site is made of Ni for $x = 5.14$ but contains 25% Mn for $x = 5.50$. This shows that, according to the nature of the substituent, the composition of the dumbbells can be very different. However, it is concluded that the dumbbell atoms are not in contact because no reliable information on their nature can be obtained from their distances along the **c** axis.

CONCLUSION

The crystal structures of the compounds LaNi$_{4.4}$Cu, LaNi$_5$Cu, and LaNi$_{4.5}$Cu$_{1.5}$ have been fully determined by means of anomalous synchrotron X-ray and neutron diffraction using joint Rietveld refinement. This powerful method has allowed us to characterize the nonstoichiometry of these AB_x compounds ($5 < x \leq 6$) in terms of dumbbells of B-type atoms, replacing the A-type atoms and to obtain with good accuracy the nickel-to-copper ratio over the different available B-type sites in the structure. Accurate knowledge of the crystal structure of such compounds using

a combination of two different diffraction techniques is of importance in regard to their potential application as negative electrode materials.

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