ESRF	**Experiment title: Localisation of copper in over-stoichiometric $La(Ni,Cu)_{5+x}$ type compounds by means of anomalous diffraction.**	**Experiment number: CH-337**
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Report:

Introduction

AB_5-type hydride forming compounds have attracted serious commercial interest in the last few years due to their widespread application in rechargeable nickel metal hydride (Ni-MH) 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 within the AB_5 stoichiometry. This resulted in multicomponent compounds [1]. Recently it has been shown that the electrochemical cycling stability can also be improved by employing so-called over stoichiometric compounds [2]. These AB_x compounds (x>5), which contain an excess of B-type elements can easily be prepared by substituting part of the La atoms in the crystal by dumbbell pairs of B-type atoms. It has been observed that Cu plays an important role in the stability of these compounds. Classical powder X-ray diffraction data (XRD) of the $La(Ni,Cu)_x$ system indicate from cell parameter variations that the dumbbells probably consist of nickel atoms only, while the Cu atoms occupy a six fold positions around these dumbbells [3].

However, the absence of contrast from classical X-ray between copper and nickel does not allow to fully solve the structure. Attempt to refine the structure from neutron diffraction data [4] leads to unreliable results related to instability of the refinement. Recently, the site occupancies in the compound $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ were investigated with success using multiwavelength synchrotron powder diffraction [5]. We therefore used the high resolution from anomalous synchrotron powder diffraction coupled with the neutron diffraction data to fully determine the structure of the over-stoichiometric Cu-containing compounds especially in terms of copper to nickel substitution ratio.

Diffraction experiments

The synchrotron diffraction patterns have been collected at the Powder Diffraction Beam Line BM16. The samples were prepared in flat-plate geometry according to their high absorption coefficient ($\mu \approx 1710\ cm^{-1}$ at 83 17 eV). The circular sample holders were filled with a paste made of 95 wt. % of powdered sample ($<36\mu m$) and 5 wt.% of polytetrafluoroethylen (PTFE) in solution. This preparation allows an excellent flatness of the surface, a good statistic of the grain orientation and a perfect cohesion of the powder versus 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 ($\lambda=1.4905$ A) corresponds to an energy lying at -9 eV ($E=8318\ eV$) below the K-edge of Ni ($E=8327$ eV) as measured by fluorescence on the first studied sample $LaNi_{5.4}$ (i.e. at -14 eV below the K edge of the free atom (E=8332 eV)). The exact value of the wavelength (i.e. the energy) was determined with a silicon standard and the efficiency of the nine detectors was checked with a corundum sample. The f' and f'' values for each element were calculated using the method of Cromer & Libermann. The data treatment was carried out in a joint Rietveld refinement between neutron and synchrotron data using the program GSAS.

Results

The crystal structures of the compounds $LaNi_4Cu$, $LaNi_{4.4}Cu$, $LaNi_{5.0}Cu$ and $LaNi_{4.5}Cu_{1.5}$ have been fully determined by means of synchrotron anomalous X-ray and neutron diffraction using joint refinement. This method has allowed to characterise the over-stoichiometry of these AB_x compounds ($5 \leq x \leq 6$) in terms of dumbbells of B atoms replacing the A ones and to obtain with good accuracy the nickel to copper ratio over the different available B sites in the structure. This breakthrough in the crystal structure of such compounds is of importance in regard to their potential application as negative electrode materials.

References

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