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HAADF and EELS Combined Studies of a New Generation of Materials for Ni-MH Batteries

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Applications for Ni-MH batteries are driven by increased energy density. Hydride forming compounds such as La–Mg–Ni ternary compounds show improved performance, in particular new crystallographic phases of A_2B_7 type [1,2,3]. Such compounds can be described as the growth along the c axis of two different sub-units [AB_5] (*C* layer) and [A_2B_4] (*L* layer), where A is a rare earth or an alkali earth and B is a transition metal, forming either a rhombohedral [3*R*] (*R*-3*m*) or hexagonal [2*H*] ($P6_3/mmc$) crystallographic structure. A series of compounds in this family of materials has been prepared by spark plasma sintering (SPS) and characterized by X-ray, microprobe and TEM analysis.

Here we present analysis of a $La_{0.65}Nd_{0.15}Mg_{0.20}Ni_{3.5}$ compound by HREM, HAADF and STEM EELS in order to identify the local structure and defects. HRTEM observations were performed on an image-corrected FEI Tecnai (SACTEM-Toulouse) operating at 200 kV and HAADF imaging and STEM EELS on a probe-corrected FEI Titan 60-300 microscope operating at 300 kV (Zaragoza).

Assuming the intensity of the columns can be related to the *Z* atomic numbers of the different elements in presence (Nd:60, La:57, Ni:28, Mg:12), the structure can be interpreted readily from the HAADF image from Fig. 1. In particular, the highest intensity can be identified as the rare-earth columns, and the layers lacking contrast the nominally Mg_2Ni_4 layers. The fact that the Mg_2Ni_4 layer are visible at all, suggests that rare-earth elements are indeed also present here. This is confirmed by X-ray analysis showing that Mg partially substitutes rare-earth elements only in the [A_2B_4] layer. The contrast allows us to identify the structure in this grain as the rhomohedral [3*R*] structure in agreement with the majority phase determined from Rietveld analysis of the X-ray diffraction patterns. As expected, the Ni sublattice is less identifiable, though the columns with two superposed Ni atoms in the unit cell are clearly visible. The intensity profile along the Ni atom line (in red on Fig 1), which is superimposed to the HAADF image, is of help to discriminate single and superposed Ni atoms. The simulation fits quite well the image, but the exact position of La and Nd atoms remains unclear (close *Z* values). Spatially resolved STEM EELS cartography will be presented to conclude on that point and on the chemical nature of occasional changes in the sequence of stacking. The spatially resolved EELS analysis will be helpful to accurately interpret the contrast in the HAADF images.

References

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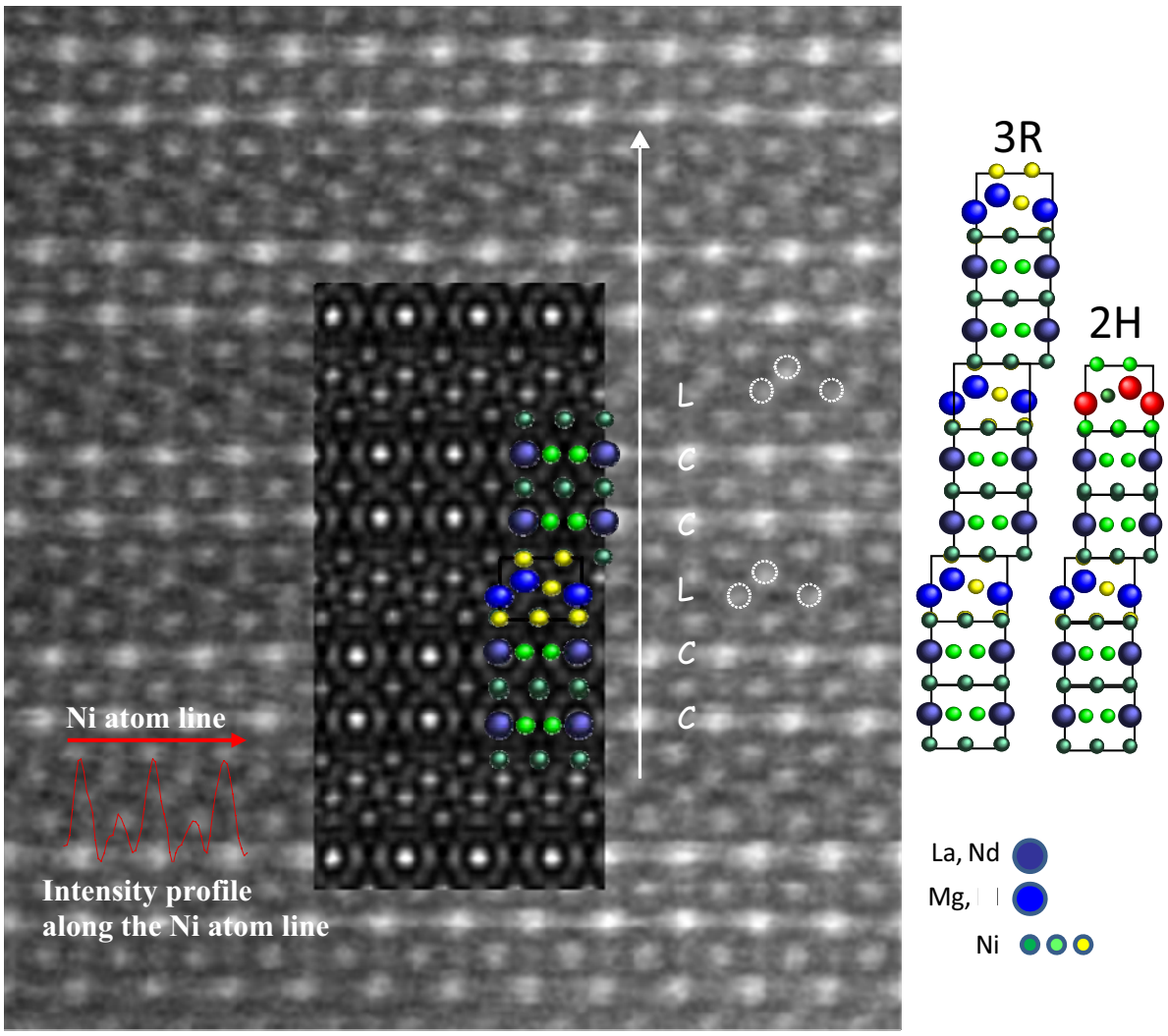

FIG. 1. : Ultra high magnification HAADF image of the $La_{0.65}Nd_{0.15}Mg_{0.20}Ni_{3.5}$ sample. A simulation and the structure are superimposed. The intensity variation along a Ni line (indicated by a red arrow) is also superimposed. The image has been Wiener filtered.

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