

Direct Imaging of Interstitial Atoms in a Complex $(\text{La}_{0.6}\text{Er}_{0.4})_5\text{Ni}_{19}$ Hydrogen-Storage Compound

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RE_mNi_n -based complex compounds (RE: rare earth, $2 < n/m < 5$) have attracted increasing attentions as novel hydrogen-storage materials or negative electrode materials of Ni-MH batteries. These compounds are constructed by the stacking of the “structural blocks”, which are represented by Haucke-unit (RENi_5) and Laves-unit (RE_2Ni_4) with their stacking ratio of $p : q$ ($[p, q]$ -type, where $x = n/m = (5p+4q)/(p+2q)$) [1]. Partially substituting the La site with X element (*i.e.*, Mg) in the La_mNi_n compounds led to significant improvements of the hydrogen-storage properties [2]. Therefore, it is essential to understand the role of dopant X atoms, including their favorable substitution sites, lattice defects and how they alter lattice structure. These local behaviors should be closely related to the hydrogen-storage properties. Using atomic-resolution STEM combined with EELS (JEOL, C_s -corrected ARM-200F operated at 200 kV), we investigate atomic structure of a $(\text{La}_{0.6}\text{Er}_{0.4})_5\text{Ni}_{19}$ ($X = \text{Er}$) compound, which in fact reveals the improved hydrogen-storage property.

On the basis of electron diffraction analysis, the structure of $(\text{La}_{0.6}\text{Er}_{0.4})_5\text{Ni}_{19}$ compound is identified as non-stoichiometric $[4, 1]$ -type ($x = 4.0$), despite the fact that the present compound should form a $[3, 1]$ -type structure ($x = 3.8$) given with its ideal stoichiometry. Non-stoichiometric formation of the $[4, 1]$ -type structure suggests that the present compound involves intrinsic Ni-deficiency. During STEM observation, it is found that point defects were randomly induced by electron-beam irradiation. As marked by the arrowheads in FIG. 1(a), extra Z-contrast intensities are frequently observed at interstitial positions. These extra intensities may presumably be attributed to the heavy RE atoms ($\text{La} = 57$, $\text{Er} = 68$), since their intensities are almost comparable with those of the fully-occupied Ni-atom columns ($\text{Ni} = 28$). These interstitial intensities become much more obvious in the LAADF image of FIG. 1(b), by accompanying intensity increase also for the RE- or Ni-sites those surrounding the relevant interstitial sites. This suggests that these RE- or Ni-atom columns are slightly distorted by the location of interstitial atoms. These interstitial atoms tend to localize within Laves-units or near the boundaries between Haucke- and Laves-units, as shown in FIG. 1(c). To elucidate the local chemistry of interstitial defects, we performed atomic-resolution EELS imaging (FIG. 2(a)–(c)). At the damaged (interstitial-defect) regions, local La/Er-atomic configurations show disorder, although La/Er atoms at non-damaged regions are well ordered at Haucke/Laves-units, respectively. The La/Er chemical disorder at the damaged regions suggests La atoms are diffused into the original Er sites, perhaps being via the observed interstitial positions. Generally, RE atoms are too large to occupy such interstitial sites; though, the intrinsic vacancies for the present non-stoichiometric compound possibly promote the vacancy-mediated interstitial diffusion. We will discuss details of this diffusion mechanism in terms of beam radiation effects, including local specimen heating and/or knock-on atomic displacements.

References

- [1] Y. Khan, *Acta Crystallogra. B* 30 (1974) 1533.
- [2] K. Kadir, et al., *J. Alloys Compd.* 287 (1999) 264.

- [3] This work was supported by Research Fellow of the Japan Society for the Promotion of Science (JPSJ).

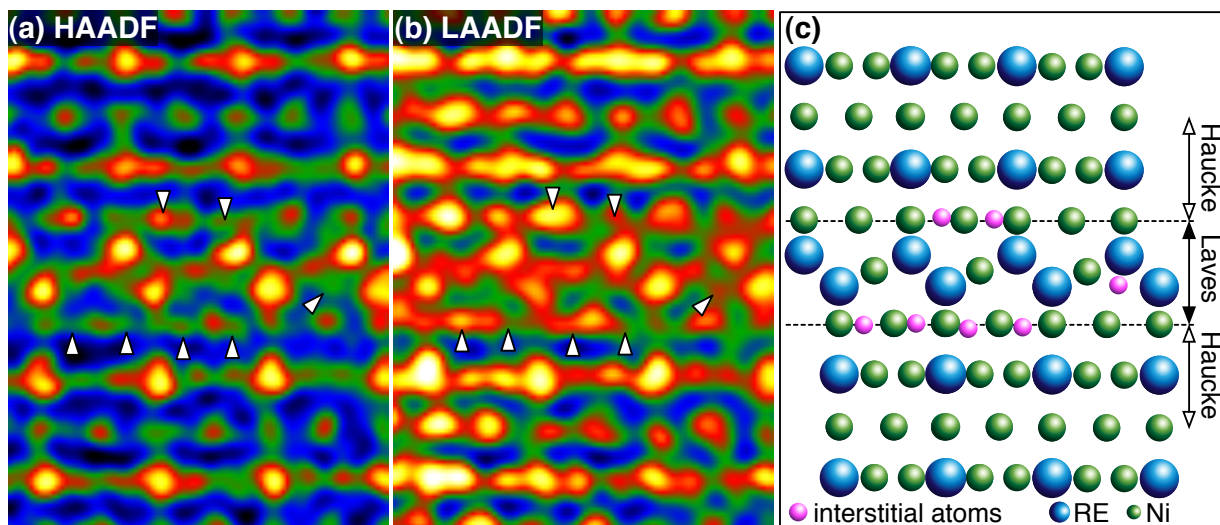


FIG. 1. (a), (b) Simultaneously recorded HAADF (70–150 mrad) and LAADF (22–70 mrad) STEM images of $(\text{La}_{0.6}\text{Er}_{0.4})_5\text{Ni}_{19}$ compound, and (c) corresponding structural model, where white arrowheads and red spheres indicate interstitial atomic sites.

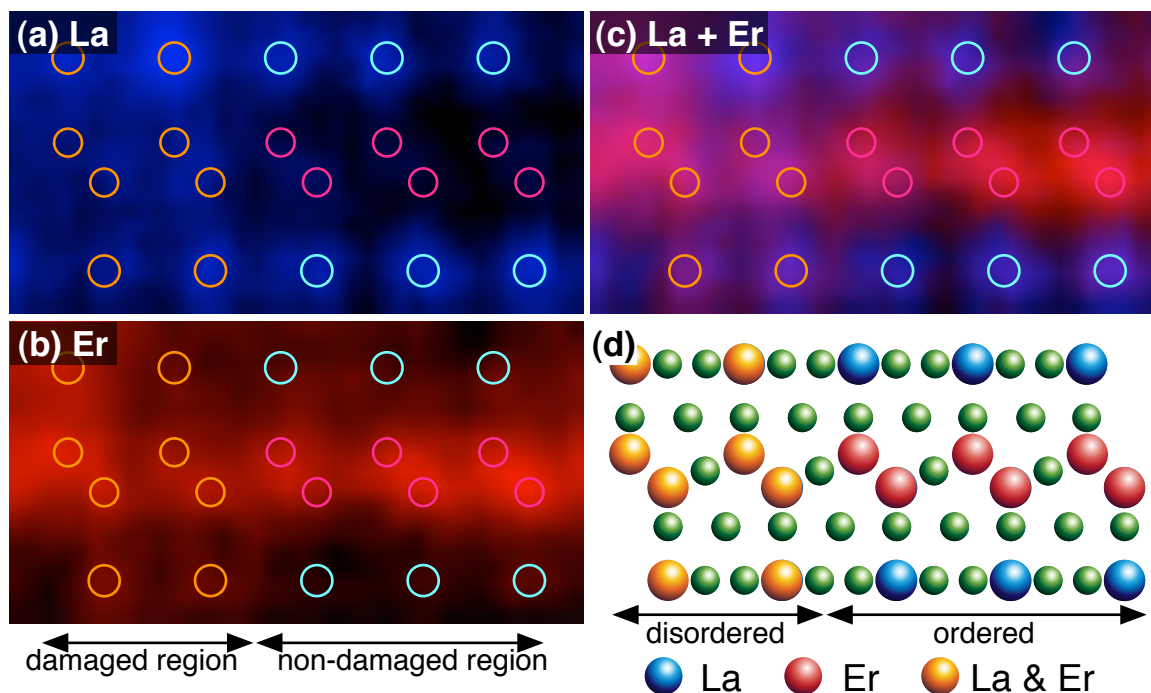


FIG. 2. (a)-(c) EELS chemical maps of La (M-edge), Er (M-edge) and La + Er, respectively. The left-hand side is damaged (interstitial defect) region and right-hand side is non-damaged region. (d) Structural model with La (blue), Er (red) and La and Er (tangerine).