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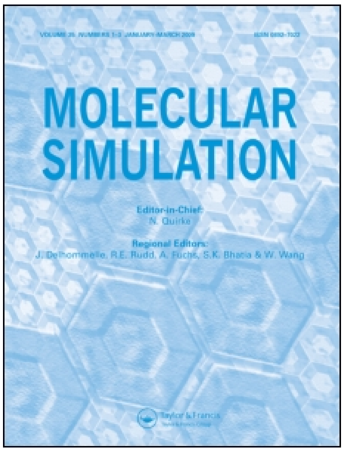

Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Hydrogen sites occupation in α-$LaNi_4Al$ hydride

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To cite this Article Zhang, R. J. , Wang, Y. M. , Lu, M. Q. , Chen, D. M. and Yang, K.(2005) 'Hydrogen sites occupation in α-$LaNi_4Al$ hydride', Molecular Simulation, 31: 14, 1101 — 1106
To link to this Article: DOI: 10.1080/08927020500371282
URL: http://dx.doi.org/10.1080/08927020500371282

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Molecular Simulation, Vol. 31, No. 14–15, 15–30 December 2005, 1101–1106

Hydrogen sites occupation in α-$LaNi_4Al$ hydride

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(Received September 2005; in final form September 2005)

The hydrogen sites occupation in $La_2Ni_8Al_2H$ has been investigated by a first-principle calculation to study the effect of the Al atom on the location of hydrogen and to explore the dominating factors to determine the hydrogen sites. It is found that the hydrogen cannot be stationed at interstitial sites surrounded by atoms including Al. Judged from the solution energy of hydrogen, the 12n site is most stable and the 4h site cannot accommodate H. The hydrogen occupation in $LaNi_4Al$ shows a distinct way from that in $LaNi_5$, where five nonequivalent interstices (3f, 4h, 6m, 12o, 12n) have been reported to be available for the hydrogen in $LaNi_5$. This indicates that the Al atom has important influence on the hydrogen occupation. The $\mathbf{BO^{s}_{H-Ni}}$ seems to be a parameter to measure the stability of $La_2Ni_8Al_2H$. By analyzing the density of states combined with the local environment of sites, the bond order (BO) and average Mulliken charge (AMC), we found that the 12n and 3f sites have similar atomic and electronic structure and the covalence and ionicity. The 3f site is also favorite occupation for hydrogen besides the 12n site.

Keywords: Hydrogen occupation; First-principles calculation; $La_2Ni_8Al_2H$; Electronic structure; Covalence; Ionicity

1. Introduction

$LaNi_5$ and related compounds have attracted much attention all over the world for a few decades because of their ability to form reversible hydrides as hydrogen storage materials [1,2] and other widely-used applications [3,4] such as the $Ni-MH_x$ battery. Many researchers have focused on the substitution alloys $LaNi_{5-x}M_x$ (M = Al, Mn, Fe, Co, and Cu, etc.) [5–8] because the absorption and desorption characteristics of $LaNi_5$ can be improved by these substitution atoms. Knowledge of the crystallographic structure is of great importance in many cases and several techniques especially neutron-powder diffraction have been repeatedly used to determine the hydrogen occupation positions in the crystal lattice. A number of studies [9–17] have been mostly reported on the β phases of these hydrogen storage materials. There are still a few studies [18] on α phase of $LaNi_5$–H system though it is difficult to prepare crystals of the phases. But many results on the preferred hydrogen occupation sites are still controversial. The 12n and/or 3f sites have been considered as the preferred occupation sites in refs. [19–21]. Hempelmann *et al.* [22] reported that both 3f and 6m are occupied. The recent work by Nakamura *et al.* [16] concluded that the 6m site is the most preferred. However, they performed first-principles calculation on a rigid-sphere model based on the TB-LMTO-ASA method and did not optimize the structure. The well known empirical geometric criterion [12,23,24] for the interstitial occupation of hydrogen was considered by Gross *et al.* [15] and they predicted that the 6m and 12n sites are occupied in the α solid solution phase of $LaNi_5H_{<1}$. This geometric criterion by Westlake states that the minimum interstitial size is 0.4 Å for a hydrogen atom to occupy in a stable hydride. However, Tatsumi *et al.* [25] recently drew a conclusion after careful investigation that there is no clear correlation between the initial hole radius and the stability in the optimized structures and that the stability of the interstices can be explained by the number of near-neighbor Ni atoms. These researchers all try to explain the atomic structure of α phase of $LaNi_5$–H, but α phases of $LaNi_{5-x}M_x$–H have rarely been studied. In order to study the effect of the substitution atoms on the location of hydrogen and explore the dominating factors to determine the hydrogen sites, in the present study

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Molecular Simulation
ISSN 0892-7022 print/ISSN 1029-0435 online
http://www.tandf.co.uk/journals
DOI: 10.1080/08927020500371282

we performed a first-principle calculation to study hydrogen sites occupation in $La_2Ni_8Al_2H$ (double cell of $LaNi_4AlH_{0.5}$).

The rest of this paper is organized as follows: in Section 2, our theoretical approach is described. Section 3 presents the results covering the hydrogen occupation sites in $LaNi_4Al$, corresponding electronic structure and analysis. Section 4 summarizes the main results of this study.

2. Computational method

The calculations in this paper were performed within density-functional theory, using a PW-PP method [26]. Density functional theory begins with a theorem by Hohenberg and Kohn [27,28], which states that all ground-state properties are functionals of the charge density ρ. Specifically, the total energy E_t may be written as:

$$E_t[\rho] = T[\rho] + U[\rho] + E_{xc}[\rho] \tag{1}$$

where $T[\rho]$ is the kinetic energy of a system of noninteracting particles of density ρ, $U[\rho]$ is the classical electrostatic energy due to Coulombic interactions, and $Exc[\rho]$ includes all many-body contributions to the total energy, in particular the exchange and correlation energies. Equation (1) is written to emphasize the explicit dependence of these quantities on ρ.

The charge density is given by the simple sum:

$$\rho(r) = \sum_i |\varphi_i(r)|^2 \tag{2}$$

where the sum is over all occupied molecular orbitals (MOs), φ_i.

From the wavefunctions equation (1) and the charge density equation (2), the energy components can be written (in atomic units) as:

$$T = \left\langle \sum_i^n \varphi_i \left| \frac{-\nabla^2}{2} \right| \varphi_i \right\rangle \tag{3}$$

$$\begin{aligned} U = & -\sum_\alpha^N \left\langle \rho(r_1) \frac{Z_\alpha}{|R_\alpha - r_1|} \right\rangle \\ & + \frac{1}{2} \left\langle \rho(r_1)\rho(r_2) \frac{1}{|r_1 - r_2|} \right\rangle \\ & + \sum_\alpha^N \sum_{\beta<\alpha} \frac{Z_\alpha Z_\beta}{|R_\alpha - R_\beta|} \\ & \equiv \langle -\rho(r_1)V_N \rangle + \left\langle \rho(r_1) \frac{V_e(r_1)}{2} \right\rangle + V_{NN} \end{aligned} \tag{4}$$

.

In equation (4), Z_α refers to the charge on nucleus α of an N-atom system. The first term, ρV_N, represents the electron–nucleus attraction. The second, $\rho V_e/2$, represents the electron–electron repulsion. The final term, V_{NN}, represents the nucleus–nucleus repulsion.

$$\varepsilon_{xc}[\rho] \cong \int \rho(r)\varepsilon_{xc}[\rho(r)]\mathrm{d}r \tag{5}$$

where $\varepsilon_{xc}[\rho]$ is the exchange-correlation energy per particle in a uniform electron gas and ρ is the number of particles.

The density mixing scheme was used to obtain the Kohn-Sham ground state based on the conjugate-gradient approach [29]. The generalized-gradient approximation (GGA) of Perdew–Wang form [30] was used for the electron exchange-correlation energy functional. Atomic structures were fully optimized for $La_2Ni_8Al_2H$ using Pulay scheme leading to a more rapid convergence. A finite basis set correction was applied to the total energy and stress tensor when a geometric optimization of variable cell parameters was made. The pseudopotentials were constructed for neutral atoms as described in the report [25]. The La-4f orbital was, therefore, not included. In fact, the contributions of La-4f to the interactions between atoms were proved to be so small that they were ignored in the PW-PP calculations and the covalent density analysis in other study [31]. The much more transferable ultrasoft pseudopotentials [32] were constructed for all ions, i.e. H, La, Ni and Al. The ultrasoft potential for these elements was recently reported to have a great advantage for an accurate description of them in complex solids [31,33]. The plane-wave cutoff of 400 eV was used for all hydrides to guarantee a good convergence with respect to the total energy E_t and the heat of formation [25,31]. The Monkhorst–Pack k-point sampling technique [34] was employed for numerical integration. For all structures, the electronic degrees of freedom were converged to 10^{-6} eV/atom, and the force components on each atom were relaxed to less than 10^{-3} eV/Å.

The formation energy ΔH of $La_2Ni_8Al_2H$ was expressed as

$$\begin{aligned} \Delta H = & \frac{1}{2} E_t[La_2Ni_8Al_2H] \\ & - \left(E_t[LaNi_4Al] + \frac{1}{4} E_t[H_2] \right) \end{aligned} \tag{6}$$

where E_t is the total energy calculated for the equilibrium unit formula shown in the parenthesis. In the structures of $La_2Ni_8Al_2H$, La atoms occupy the 1a site while the two types of Ni atoms are located, respectively, at the 2c ($z = 0$) and 3g ($z = 1/2$) sites and Al atoms occupy predominantly the 3g sites according to neutron scattering data [11,35]. Calculations of these hydrides were made by optimizing all degrees of freedom including cell parameters and internal coordinates within a given space group.

3. Results and discussion

3.1 Hydrogen occupation sites in $LaNi_4Al$

For investigating the stability of hydrogen atoms at different interstitial sites (table 1) in $LaNi_4AlH_{0.5}$, we made calculations for a double cell of $LaNi_4AlH_{0.5}$ with

Table 1. The calculated formation (solution) energy (ΔH) and cohesive energy (E_{coh}) for $La_2Ni_8Al_2H$, where hydrogen atoms are at five different interstitial sites corresponding to the Wyckoff positions 12n, 3f, 6m, 12o and 4h, respectively.

Occupied sites	*12n*		*3f*		*6m*		*12o*		*4h*
Initial sites	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*b*
Coordination	La × 1,Ni1 × 2, Ni2 × 1	La × 1,Ni1 × 2, Al × 1	La × 2,Ni1 × 2, Ni2 × 2	La × 2,Ni1 × 2, Al × 2	La × 2, Ni2 × 2	La × 2,Ni2 × 1, Al × 1	La × 1,Ni1 × 1, Ni2 × 2	La × 1,Ni1 × 1,Ni2 × 1, Al × 1	Ni1 × 1,Ni2 × 2, Al × 1
Optimized sites	a	b	a	b	a	b	a	12n(a)	12o(a)
ΔH(kJ/molH$_2$)	− 65.04	60.18	− 49.85	63.39	− 20.13	31.99	− 16.81	− 54.00	− 16.93
E_{coh} (eV/a-tom)	7.3488	7.2989	7.3427	7.2976	7.3309	7.3101	7.3296	7.3444	7.3296

a. The interstitial site in the coordination without Al atom. b. The interstitial site in the coordination with Al atom.

one H at a specific site, i.e. $La_2Ni_8Al_2H$. For Al substituting Ni at the 3g site, each of the 12n, 3f, 6m, and 12o sites have two kinds of coordination labeled by ‘a’ and ‘b’ in table 1. Ni1 and Ni2 represent Ni at the 2c and 3g site, respectively. Hence, five nonequivalent interstices (3f, 4h, 6m, 12o, 12n) in $LaNi_5$ turn to nine nonequivalent interstitial sites, whose positions are given in table 1. This table also lists the calculated formation energy and cohesive energy, the initial sites and its corresponding coordination as well as the types of sites after the geometry optimization. Of these sites, 12o(b) and 4h(b) for hydrogen occupation move to 12n(a) and 12o(a), which indicates that it is difficult for hydrogen atom to be stationed at these two original sites. It is interesting to notice that each equilibrium structure with the hydrogen atom surrounded by Al atom has a quite positive value of formation energy. That is to say, the hydrogen atom has a remote possibility to be at interstitial sites in the coordination with Al atom in despite of even a large hole radius, which means that hydrogen tends to be kept away from Al atom. It indicates that the hydrogen occupation sites have a crucial correlation with the interaction between hydrogen and its surrounding atoms. Comparing the left possible four hydrogen occupation sites, which are 12n(a), 3f(a), 6m(a) and 12o(a), we noticed that the most stable position is the 12n(a) site with the most negative value of formation energy, i.e. − 65.04 kJ/molH$_2$. Figure 1 shows the four possible sites and the 4h site in the crystal structure of $La_2Ni_8Al_2$. The following discussion will be on these four possible sites with omitting the label (a). More information can be obtained from table 1 that the predicted relative stability is 12o $<$ 6m $<$ 3f $<$ 12n, whereas the 4h site cannot accommodate H. This is a distinct way from the case of $LaNi_5$ [15,16,25], where five nonequivalent interstices (3f, 4h, 6m, 12o, 12n) have been reported to be available for the hydrogen in LaNi5. Therefore, it indicates that the Al atom has important influence on the behavior of hydrogen occupation for $LaNi_4Al$.

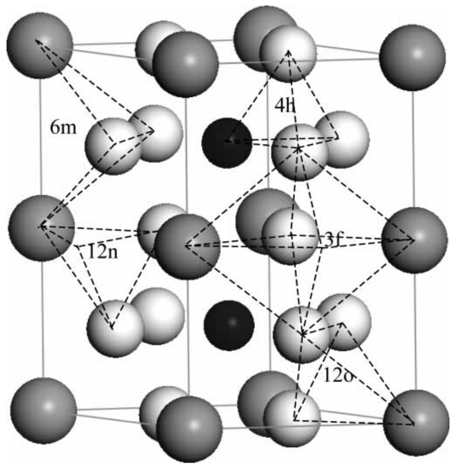

Figure 1. Schematic double cell of $LaNi_4Al$, i.e. $La_2Ni_8Al_2$. The interstitial sites are labeled as 12n, 3f, 6m, 12o, and 4h. The La, Ni, and Al atoms are characterized by gray, white and black color, respectively.

In $La_2Ni_8Al_2H$, there is only 0.04 Å distance between the 12n and 3f site after optimization and they have similar local environment. It is similar with the case in $La_2Ni_{10}H$ that the 12n site after optimization is located only 0.35 Å away from the 3f site and the 12n site was considered as an octahedral interstitial site [25]. Therefore, the 12n site in $La_2Ni_8A_{12}H$ should be more described as an octahedral interstitial site located slightly off center because of its shorter distance away from the 3f site. A hypothesis [25] is proposed that the number of Ni–H bonds at the near neighbor is an important parameter to determine the stability and the results are consistent with it on the whole in this reference. But the hypothesis does not work for the primary solid of $La_2Ni_8Al_2H$ in the present study. The number of near neighbor Ni atoms is 3, 4, 2 and 3 for 12n, 3f, 6m and 12o, respectively. We cannot find such a correlation between the solution energies of these sites and the number of near neighbor Ni atoms. In fact, the stability of H occupation sites can only be understood in terms of nature of chemical bonding between the H atom and its surrounding atoms, which is described in the following sections.

3.2 *Density of states*

The plots of partial density of states (PDOS) for a H-s part, a Ni-d part, a La-spd part and an Al-sp part, which are the main contributors to the local density of states (LDOS), of α-$La_2Ni_8Al_2H$ with four possible sites, are shown in figure 2. Below E_F (that is set to zero as a reference) there is a hybridization interaction of s, p and d orbital between atoms. The states below E_F consist mainly of the Ni-d band. However, the contributions of La-spd and Al-sp bands cannot be ignored. In order to show the bonding and anti-bonding states between H and other atoms clearly, the enlarged H 1s PDOS peaks are plotted in figure 3. Combining figure 2 with figure 3, we can see that the weaker metal bands interact with the stronger H 1sσ band and a stronger bonding state is formed. The anti-bonding state is also formed near but below E_F by the interaction between the weaker the H 1sσ* band and the stronger metal bands. It indicates from figure 2 that in $La_2Ni_8Al_2H$ there is not a diversification for the La, Ni and Al metal PDOS peaks for the four sites, but H 1s peak has a discernable change for them. Moreover, this kind of change is especially shown in the H 1sσ band in figure 3. The H 1sσ peaks of 12n and 3f are similar, correspondingly with the similar environment around the H atom and the near distance between the two sites. Figure 3 also displays more H 1sσ split peaks of 6m and 12o than the other two. And they have a shift to the high energy region.

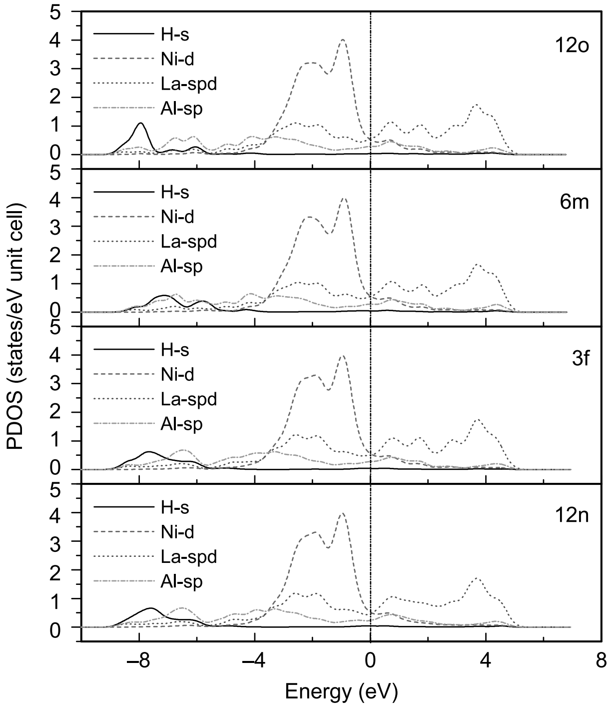

Figure 2. The PDOSs of α-$La_2Ni_8Al_2H$ with four possible hydrogen sites. E_F is referenced as zero.

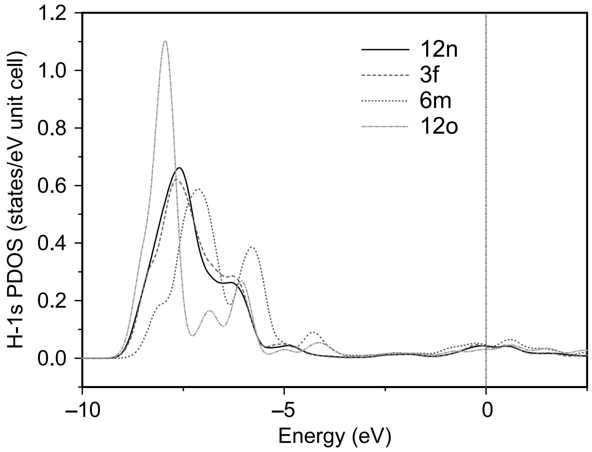

Figure 3. The H-1s PDOSs of α-$La_2Ni_8Al_2H$ with four possible hydrogen sites. E_F is referenced as zero.

In order to measure the interaction of H and metal atoms quantitatively, table 2 gives the average bond order (BO) [36], bond length (BL) and scaled bond order (BO^s) between H–Ni, H–La and H–Al for $La_2Ni_8Al_2H$ with the four sites. The BO^s, $BO^s_{H-Ni\,(or\,La,Al)} = BO_{H-Ni\,(or\,La,Al)}/BL_{H-Ni\,(or\,La,Al)}$, provides an objective criterion for bonding between H–Ni, H–La and H–Al for $La_2Ni_8Al_2H$. It indicates that the scaled bond orders between H and Ni for the models with 12n and 3f are closer and higher than those for the latter two. The BO^s_{H-Ni} decreases in the order of 3f, 12n, 6m and 12o, in agreement with the general trend of the stability except for the case of 12n. The $BO^s_{H-La\,or\,Al}$ or Al cannot display such a relation. Furthermore, a negative value of BO^s shows no bonding interaction between H and La or Al. The electronic structures of hydrides for $LaNi_5$ and its substitutional alloys [37,38] has been calculated, which shows that the interaction between the H and Ni atoms is

Table 2. The average BO, BL and BO^s between H–Ni, H–La and H–Al for $La_2Ni_8Al_2H$ with the four possible hydrogen sites.

	H–Ni			*H–La*			*H–Al*		
	BO	*BL*	*BO^s*	*BO*	*BL*	*BO^s*	*BO*	*BL*	*BO^s*
12n	0.248	1.839	0.135	− 0.590	2.510	− 0.235	0.000	3.268	0.000
3f	0.265	1.810	0.146	− 0.590	2.511	− 0.235	0.000	3.244	0.000
6m	0.170	2.108	0.081	− 0.170	2.465	− 0.069	0.000	2.916	0.000
12o	0.158	2.177	0.073	− 0.490	2.354	− 0.208	− 0.040	2.594	− 0.015

dominating in the metal–hydrogen bonding states. Therefore, $\mathrm{BO}^{s}_{\mathrm{H-Ni}}$ seems to be considered as a parameter to measure the stability of $La_2Ni_8Al_2H$.

3.3 *Covalence and ionicity analysis*

The average Mulliken charge (AMC) [36,39] on H, Ni Al and La atom for $La_2Ni_8Al_2H$ with the four sites listed in table 3 is used to measure the ionicity. It shows that H, Ni and Al are always electron acceptors; La is always an electron donor. We found that the AMC on H, Ni, and La for 12n is close to 3f and quite different from 6m and 12o. This confirms the results and discussion in the above description that the 12n and 3f sites have similar atomic and electronic structure. However, it is not applicable for the AMC on Al. Furthermore, the change of AMC on Al due to the different hydrogen site is smaller than that on other atoms. The reason is that the H atom is far away from the Al atom and not positioned at the interstitial site surrounded with Al. It can be inferred from table 3 that the ionicity of H increases in the order of $12n = 3f < 6m < 12o$. It is in accordance with the decrease of both the $\mathrm{BO}^{s}_{\mathrm{H-Ni}}$ and the stability except for the inequality between 12n and 3f, but the cases of the two sites are always close to each other. Therefore, by analyzing the AMC on atoms combined with the $\mathrm{BO}^{s}_{\mathrm{H-Ni}}$ and the local environment of sites, it can be inferred that the 3f site is another favorite occupation for hydrogen besides 12n.

4. Conclusion

The behavior of the hydrogen occupation in $La_2Ni_8Al_2H$ has been investigated by first-principles calculations including the structures geometry optimization. It shows that the hydrogen tends to be kept away from the aluminum atom and cannot be stationed at interstitial sites surrounded by Al atom. The 4h site cannot accommodate H. Thus, the hydrogen in $LaNi_4Al$ shows a distinct way from that in $LaNi_5$, where five nonequivalent interstices (3f, 4h, 6m, 12o, 12n) have been reported to be available for the hydrogen in $LaNi_5$. This indicates that the Al atom has important influence on the hydrogen occupation. From the viewpoint of energy, the 12n site is most stable according to its most negative solution energy of hydrogen in $LaNi_4Al$. $\mathrm{BO}^{s}_{\mathrm{H-Ni}}$ seems to be a parameter to measure the stability of $La_2Ni_8Al_2H$. By analyzing the density of states combined with the local environment of sites, the BO and AMC, we found that the 12n and 3f sites have similar atomic and electronic structure and the covalence and ionicity. It can be concluded that the 3f site is another favorite occupation for hydrogen besides the 12n site.

Table 3. The AMC on H, Ni, Al and La for $La_2Ni_8Al_2H$ with the four possible hydrogen sites.

	H	*Ni*	*Al*	*La*
12n	− 0.240	− 0.434	− 0.145	2.000
3f	− 0.240	− 0.438	− 0.140	2.005
6m	− 0.250	− 0.455	− 0.135	2.080
12o	− 0.260	− 0.444	− 0.145	2.045

Acknowledgements

The authors are grateful to Dr D.S. Xu, department of Titanium Alloys, Shenyang advanced material R&D center, at this laboratory for computer resources and helpful discussions.

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