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A first-principles study of the La–H system

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ABSTRACT

Results from first-principles investigations of the structural, electronic, and vibrational properties for three concentration ranges (stoichiometries close to elemental La, LaH_2, and LaH_3) within the La–H system are presented.

1. Introduction

The binary La–H system is of great interest, because of a concentration-dependent metal–insulator transition at a composition near $LaH_{2.8}$ [1] and the "switchable mirror" phenomenon for thin La films [2]. However, not much is known about details of the crystal structure and of the phase diagram as well as the mechanism of the metal–insulator transition.

Elemental La exists as a double-hexagonal close-packed (dhcp) phase below ~310 °C. The homogeneity range of the solution of H in the dhcp phase is very narrow. LaH_2, which shows metallic behaviour, crystallizes in the fluorite structure with all tetrahedral interstices of the fcc La lattice occupied and all octahedral sites vacant. As additional H is incorporated in the octahedral interstices of the La lattice, a composition of LaH_3 is reached. However, these octahedral H atoms of the cubic LaH_{3-x} phase ($x > 0$) are generally not located in the centres of the metal–atom octahedra [3], but are displaced along the $\langle 1\,1\,1 \rangle$ direction towards the tetrahedral interstices. In $LaH_{2.96}$ these displacements are as large as 0.37 Å [3] and lead to a pronounced shortening of the La–H bonds. This effect has been related to the size of the rare-earth atom and the compositional range of the cubic fcc phase [4]. Recently [5] it has been shown that displacements of octahedral H atoms of this magnitude may be caused by H vacancies in adjacent tetrahedral interstices for which the presence of a few percent cannot be excluded by standard experimental techniques.

For the present investigation we have performed first-principles calculations for ordered model structures. For the dhcp lattice they have been obtained from the $2 \times 2 \times 1$ and $3 \times 3 \times 1$ supercells of the conventional unit cell (containing 16 and 36 La atoms, respectively) and for the fcc lattice from either the $2 \times 2 \times 2$ supercell of the cubic unit cell (32 La atoms) or a rhombohedral cell with 16 La atoms spanned by the basis vectors resulting from considering the 32-atom cell as formally being body centred. The H atoms have been placed at the tetrahedral and/or octahedral sites; structure optimizations and total-energy calculations have been performed.

2. First-principles calculations

For the performed structure optimizations and total energy calculations the Vienna ab initio simulation package (VASP)

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[6–8] has been used. By this method the Kohn–Sham equations of density functional theory (DFT) [9,10] with periodic boundary conditions are solved within a plane-wave basis set with electron–ion interactions described by the projector augmented wave (PAW) method [11,12]. The applied lanthanum PAW potential includes 5s5p6s5d4f. Exchange and correlation have been treated within the generalized gradient approximation (GGA) by Perdew et al. [13]. Reciprocal space sampling has been performed using Monkhorst–Pack k-meshes [14] and reciprocal-space integration has been performed by the linear tetrahedron method [15,16] including the Blöchl correction [17]. Optimization of structural parameters has been achieved by minimization of atomic forces and stress tensors applying the conjugate gradient technique.

A reference energy for H_2 has been obtained by consistently computing the VASP total energy of a single H_2 molecule in a sufficiently large otherwise empty simulation cell to exclude interactions between translation-symmetry copies; the H–H bond length has been optimized.

Phonon dispersions have been calculated from first principles by the direct method using the MedeA-Phonon software [18].

Electron densities have been calculated with the full-potential linearized augmented plane-wave (FLAPW) method (see [19] and references therein) using an exchange-correlation potential by Hedin and Lundqvist [20].

3. LaH_x, $x \le 0.125$

For elemental La the dhcp structure has turned out to be vibrationally and energetically stable at zero temperature. We have probed compositions from pure La to $LaH_{0.125}$ by inserting one or two octahedral or tetrahedral H atoms into the dhcp La_{36} and La_{16} cells as well as into the fcc La_{32} and La_{16} cells. The resulting 79 structures have been optimized and their total energies have been calculated.

Comparing phonon dispersions for dhcp $La_{36}H$ with fcc $La_{32}H$ on the one hand and dhcp with fcc $La_{16}H$ on the other hand, it has turned out that for the lower H content ($La_{36}H$ and $La_{32}H$: $c_H \approx 3$ atom%) as well as for pure La the dhcp structure is vibrationally stable and the fcc structure is vibrationally unstable, whereas for the higher content in $La_{16}H$ ($c_H \approx 6$ atom%) the fcc phase is vibrationally stable and the dhcp phase is vibrationally unstable.

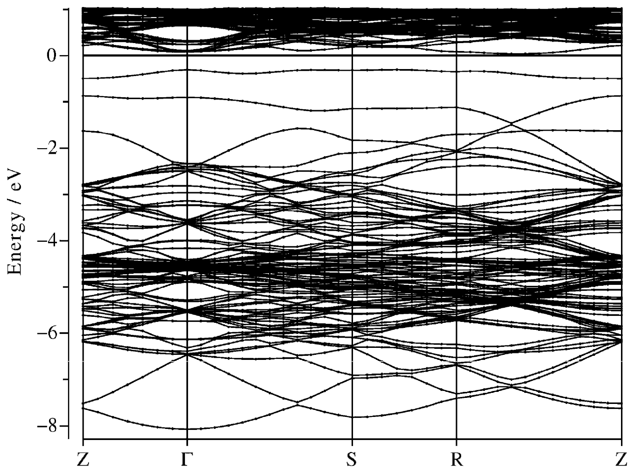

Fig. 1. Electronic band structure for $La_{32}H_{94}$ with two octahedral vacancies 3.9 Å apart (Brillouin zone corresponding to orthorhombic primitive Bravais lattice; energy scale with respect to Fermi energy).

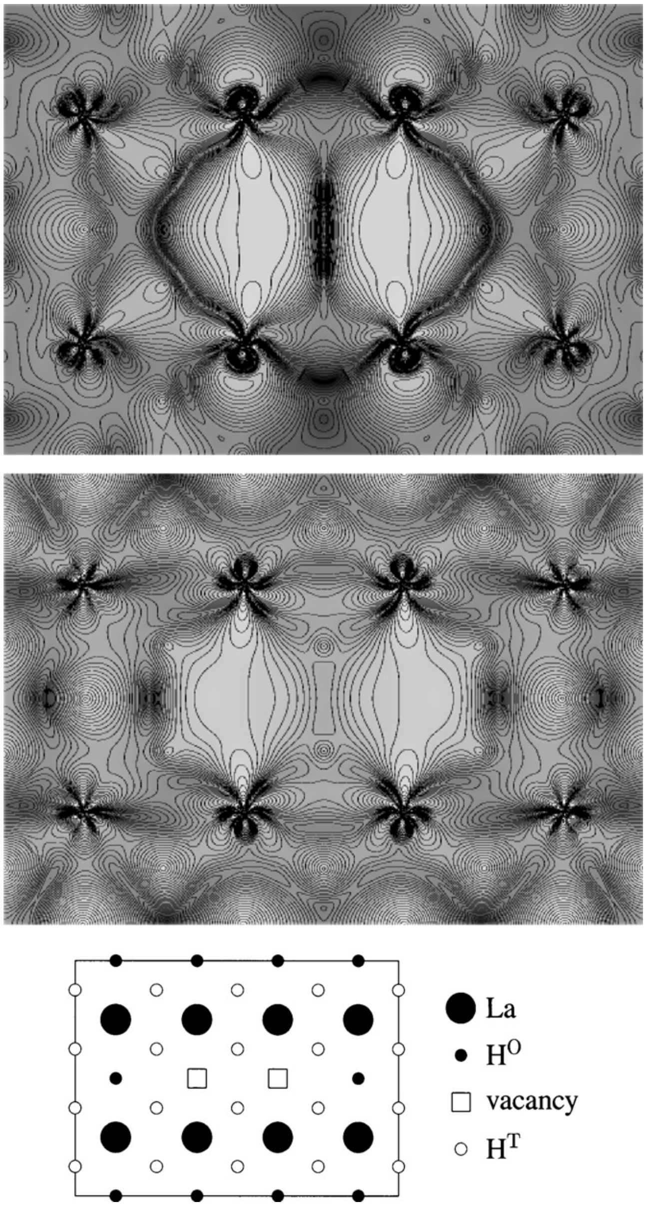

Fig. 2. Contour maps of the electron densities in the (1 1 0) plane for the first (top) and the second band (centre) below the Fermi level for $La_{32}H_{94}$ with two octahedral H vacancies 3.9 Å apart (see Fig. 1). The superimposed grey shadings may help to discern the regions of higher electron density (lighter grey areas) due to the two parallel La–La bonds across the H vacancies. The sketch at the bottom shows the positions of the atoms in the (1 1 0) plane, H^O and H^T symbolize octahedrally and tetrahedrally coordinated H atoms, respectively.

This change of the phase stability is in agreement with the change of the formation energy, i.e. the reaction energy for

$$m\,\mathrm{La}^{\mathrm{dhcp}} + \left(\frac{1}{2}\right)\mathrm{H}_2 \rightarrow \mathrm{La}_m\mathrm{H}, \quad m = 36, 32,\ 16$$

calculated from the total energies of the respective model structures and appropriate reference energies for La and for the H_2 molecule.

Furthermore – and very surprisingly – it follows from the analysis of the total energies that the occupation of an octahedral interstitial site is energetically more favourable than the occupation of a tetrahedral site by ~15 kJ/mol H_2 (dhcp model structures) or ~27 kJ/mol H_2 (fcc model structures). This does not seem to have been verified yet experimentally.

For the 71 possible structures containing 2 H atoms per La_{32} cell or La_{16} cell, linear H–La–H arrangements with La–H distances of ∼2.5 Å have turned out to be energetically favourable.

All investigated model structures have been found to be energetically destabilized by about 0.7–4.9 kJ/mol per La atom with respect to the phase segregation

$$LaH_x \rightarrow \left(\frac{x}{2}\right) LaH_2 + \left(1 - \frac{x}{2}\right) La^{dhcp}.$$

4. LaH_2 and stoichiometries close to the dihydride

Stoichiometric LaH_2 with fluorite structure is energetically stabilized by ∼35 kJ/mol per formula unit with respect to the phase separation into La^{dhcp} and LaH_3 (optimized orthorhombic structure, cf. Section 5). In addition, it is vibrationally stable.

Thirty-two model structures have been constructed based on the $La_{32}H_{64}$ cell and the rhombohedral $La_{16}H_{32}$ cell in the concentration range from $LaH_{1.875}$ to $LaH_{2.125}$.

The shift of a tetrahedral H atom in the stoichiometric dihydride to an octahedral site results in a loss of energy of ∼180 kJ/mol per H_2. Adding hydrogen to the stoichiometric dihydride releases ∼100 kJ/mol per H_2; the resulting super-stoichiometric model structures are stabilized by about 0.20–0.58 kJ/mol per La atom with respect to the phase separation into LaH_2 and orthorhombic LaH_3 (see below). Removing hydrogen requires about 270 kJ/mol per H_2; the resulting sub-stoichiometric models are destabilized by about 1.3–4.9 kJ/mol per La atom with respect to the phase segregation into LaH_2 and La^{dhcp}. The structure models for the sub-stoichiometric and super-stoichiometric dihydrides studied so far are vibrationally stable.

5. LaH_3 and stoichiometries close to the trihydride

For stoichiometric LaH_3 structure optimization for an $La_{32}H_{96}$ unit cell has led to an orthorhombically distorted structure ($Z = 4$, lattice parameters: $a = 8.010$ Å, $b = 5.289$ Å, $c = 4.079$ Å, corresponding to a change of cell dimensions of +1.9%, −4.8%, +3.3% with respect to the cubic unit cell) which is about 2.1 kJ/mol per formula unit more stable than the ideal cubic structure. The distortion is accompanied by a volume increase of ∼0.7% and by large changes in the interatomic distances. Phonon calculations show that the undistorted cubic structure is unstable and the distorted structure is stable.

Starting from the 2 × 2 × 2 supercell for LaH_3 we have removed up to six H atoms (both octahedral and tetrahedral) and performed optimizations for about 50 different structures. For $La_{32}H_{94}$ ($LaH_{2.94}$) with two octahedral H vacancies the most stable arrangement has turned out to be the one where the vacancies are 3.9 Å apart. The band structure for this model structure exhibits a band gap (Fig. 1) as expected from experiment. In Fig. 2 electron densities for the first two bands below the Fermi level are shown. These bands are mainly determined by the d states of the La atoms adjacent to the H vacancies which form bonds across these vacant sites. An analogous, but energetically less favourable bond formation leading to the opening of a band gap is always found (of course, only for cells containing an even number of electrons) when at least one octahedral H position is empty and also in the case of some structures with only tetrahedral H vacancies.

6. Résumé

For small H concentrations the occupation of octahedral interstitial sites is preferred both in dhcp and fcc La. Increasing H concentration stabilizes the cubic phase.

For stoichiometric LaH_3 a stable orthorhombic structure has been found. For stoichiometries close to LaH_3 pairs of octahedral H vacancies at the shortest possible distance (3.9 Å) are the energetically most favourable vacancy arrangements. For such pairs, as well as for many other vacancy arrangements close to LaH_3, a band gap opens. This is caused by a vacancy-induced formation of energetically favourable La–La bonds and the lowering of the respective La-d states below the Fermi level.

Further investigations aimed at a first-principles study covering the complete composition range of the La–H phase diagram are in progress.

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