

First-principles study of the solid solution of hydrogen in lanthanum

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Results from first-principles investigations of the energetical, structural, electronic, and vibrational properties of model structures probing the metal-rich region of the lanthanum-hydrogen system, i.e., the region of the solid solution of hydrogen in lanthanum, are presented. We have studied the site preference and the ordering tendency of hydrogen atoms interstitially bonded in close-packed lanthanum. Spatially separated hydrogen atoms have turned out to exhibit an energetical preference for the occupation of octahedral interstitial sites at low temperature. Indications for a reversal of the site preference in favor of the occupation of tetrahedral interstitial sites at elevated temperature have been found. Linear arrangements consisting of pairs of octahedrally and/or tetrahedrally coordinated hydrogen atoms collinearly bonded to a central lanthanum atom have turned out to be energetically favorable structure elements. Further stabilization is achieved if such hydrogen pairs are in turn linked together so that extended chains of La-H bonds are formed. Pair formation and chain linking counteract the energetical preference for octahedral coordination observed for separated hydrogen atoms.

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I. INTRODUCTION

Three allotropes are known for elemental lanthanum: The double hexagonal-close-packed (dhcp) modification is stable at temperatures below 583 K, the cubic close-packed (ccp) modification at intermediate temperatures, and the body-centered-cubic (bcc) modification at temperatures between 1138 K and the melting point at 1191 K. The homogeneity range of the solution of hydrogen in dhcp lanthanum seems to be very narrow; the width of this phase, i.e., the solubility of hydrogen in dhcp lanthanum, however, has not yet been accurately determined (cf. Ref. 1, which is, to our knowledge, the only attempt to measure the hydrogen solubility limit in dhcp lanthanum). A phase diagram of the binary lanthanum-hydrogen system assessed from experimental data can be found in Ref. 2. The solid solution is in equilibrium with lanthanum hydride, which has a face-centered-cubic structure. The stoichiometric dihydride crystallizes with fluorite (CaF₂) structure, space-group type $Fm\bar{3}m$, i.e., in an idealized picture, the hydrogen atoms of the stoichiometric dihydride completely occupy the tetrahedral interstitial sites of a matrix of ccp lanthanum atoms, leaving the octahedral interstitial sites completely unoccupied. The hydride can be continuously loaded with hydrogen beyond the dihydride composition, whereby the octahedral interstitial sites become occupied as well. The trihydride, which is assumed to have a structure of the D0₃ type (Strukturbericht designation) with $Fm\bar{3}m$ symmetry, is the hydrogen-rich boundary of the lanthanum-hydrogen system. In the concentration range between LaH₂ and LaH₃, tetragonal superstructures due to the ordering of the hydrogen atoms in the octahedral interstitial lattice,^{3–5} tetragonal distortions of the

lanthanum substructure,⁶ and displacements of the hydrogen atoms occupying the octahedral interstitial sites along the $\langle 111 \rangle$ directions^{7,8} are observed. It is worth mentioning that a first-principles structure optimization of the stoichiometric trihydride has led to an orthorhombically distorted structure with four formula units per unit cell and the lattice constants $a = 8.010 \text{ \AA}$, $b = 5.289 \text{ \AA}$, $c = 4.079 \text{ \AA}$.⁹

Considering the structure of the dihydride (the fluorite-type structure is *nota bene* a general feature of the dihydrides of the trivalent rare-earth metals) and assuming analogy between lanthanum and those rare-earth metals for which the tetrahedral sites have been proved to be preferred by hydrogen atoms at low hydrogen concentrations (see Ref. 10, p. 216, and the references therein), it may be expected for the solid solution of hydrogen in lanthanum that the hydrogen atoms preferably occupy the tetrahedral interstitial sites. In the case of the lanthanum-hydrogen system, however, the structure of the solid-solution phase has not yet been investigated by any experimental technique as far as we know.

Our present first-principles study of the metal-rich side of the lanthanum-hydrogen system is aimed at an examination of the site preference of spatially separated hydrogen atoms and of the possible formation of hydrogen pairs and more extended chainlike hydrogen arrangements in a matrix of dhcp or ccp lanthanum.

The solid solutions of hydrogen in several hexagonal-close-packed (hcp) rare-earth elements R ($R = \text{Sc, Y, Lu}$ and presumably also Ho, Er, Tm) exhibit low-temperature phases in which the interstitially bonded hydrogen atoms form short-range ordered structures. The formation of these

low-temperature phases is connected to phenomena such as anomalies in the electrical conductivity and a temperature-independent hydrogen solubility. The ordered hydrogen substructures consist of pairs of tetrahedrally coordinated hydrogen atoms collinearly bonded to a central R atom that organize themselves in a chainlike way. See Refs. 11 and 12 for recent first-principles studies of the hydrogen ordering in scandium and yttrium and Ref. 10 for a review of this subject. Preliminary results from current and yet unfinished first-principles investigations of the solid-solution phases of hydrogen in scandium, yttrium, and lutetium are anticipated in this paper in order to provide a basis of comparison.

II. COMPUTATIONAL DETAILS

A. Structure optimizations, total energy, and electronic structure calculations

Structure optimizations and total energy calculations have been performed for different series of model structures in order to investigate the relative stability of the lanthanum phases (dhcp, ccp, bcc) and of various approximants for the solid solution of hydrogen in lanthanum metal. For this task, as well as for the computation of electronic densities of states (DOS) and band structures for selected optimized model structures, the Vienna Ab-initio Simulation Package (VASP)^{13–16} has been employed. The Kohn-Sham equations of density-functional theory^{17,18} with Born–von Kármán boundary conditions have been solved within a plane-wave basis set with electron-ion interactions described by potentials constructed according to the projector-augmented-wave method^{19,20} with a $[\text{Kr}]4d^{10}$ lanthanum core, thus treating the lanthanum $4f$ states as valence states. Scalar relativistic effects (mass velocity and Darwin terms) are included. Exchange and correlation have been treated within the generalized-gradient approximation.²¹ An energy cutoff of 500 eV has been chosen for the plane-wave basis set. Spin polarization has been excluded. Reciprocal-space sampling has been performed using Γ -centered Monkhorst-Pack k meshes;²² the energy differences between the three lanthanum modifications have been calculated based on total energies, which are convergent with respect to the number of k points, whereas k meshes with nearest-neighbor spacings between 0.15 and 0.20 \AA^{-1} have been proved to be a good compromise between accuracy and computational effort for the comparison of model structures derived from the same lanthanum unit cell and have therefore been used for this task. Reciprocal-space integration has been carried out with the first-order Methfessel-Paxton method²³ with a broadening parameter of 0.2 eV. Structural parameters (lattice parameters and ionic positions) have been optimized by the minimization of the atomic forces and the stress tensor with respect to the crystallographic degrees of freedom applying the conjugate gradient technique implemented in VASP.

The minimum of the Γ -point energy (not spin polarized) of a hydrogen dimer enclosed in a sufficiently large and otherwise empty cubic unit cell (lattice parameter $a = 10 \text{\AA}$ or larger in order to exclude the interaction between translation-equivalent molecules) as a function of the bond length calculated with VASP has been used as reference energy for molecular hydrogen.

B. Phonon-dispersion relations

Phonon-dispersion relations and the corresponding vibrational densities of states (VDOS) have been calculated for selected model structures from first principles by means of the direct method²⁴ as implemented in the MEDEA-PHONON package,²⁵ which in turn makes use of VASP in order to calculate the harmonic force constants from atomic displacements in supercells. For dhcp lanthanum and model structures derived from dhcp lanthanum, $3 \times 3 \times 1$ supercells of the conventional unit cell containing 36 lanthanum atoms have been applied; for ccp lanthanum and ccp-based model structures, $2 \times 2 \times 2$ supercells of the conventional cell comprising 32 lanthanum atoms have been used; and for bcc lanthanum, a $3 \times 3 \times 3$ supercell of the conventional cell with 108 lanthanum atoms has been utilized. Phonon modes and thermodynamic functions have turned out to be unusually dependent on the quality of the reciprocal-space sampling and the plane-wave cutoff, in particular for structures based on ccp lanthanum. Results for vibrational properties of hydrogen-containing model structures have been found to be converged for ccp-based models applying $5 \times 5 \times 5$ Monkhorst-Pack meshes (0.12 \AA^{-1} spacings) and a 400-eV plane-wave cutoff. For structures derived from the dhcp phase, $5 \times 5 \times 4$ Monkhorst-Pack meshes (0.13 \AA^{-1} spacings) and a plane-wave cutoff of 325 eV have been used, a setting that we believe to be reasonably converged, although we have not been able to further validate the convergence behavior. Furthermore, anharmonicity effects have not been taken into account. From the VDOS the temperature-dependent vibrational contributions to the free energy, i.e., the zero-point energy, the vibrational energy, and the vibrational entropy, have been computed.

III. MODEL STRUCTURES

A. Construction of model cells

The present investigations of the solid solution of hydrogen in lanthanum metal are based on series of model structures constructed by the insertion of hydrogen atoms into unit cells representing dhcp or ccp lanthanum. The high-temperature bcc phase has not been considered in detail because the investigated structures with one hydrogen atom at a sixfold coordinated (quadratic bipyramidal, i.e., distorted octahedral) or at a fourfold coordinated (disphenoidal, i.e., distorted tetrahedral) interstitial site of the $2 \times 2 \times 2$ supercell of the conventional two-atom bcc unit cell are energetically very unfavorable compared to the other relevant phases. They are destabilized by about 2 eV per unit cell compared to the corresponding structures with 1 hydrogen atom in a unit cell with 16 lanthanum atoms in ccp arrangement and have transformed into ccp structures in the course of the optimization procedure along the barrier-free Bain path of tetragonal distortion.²⁶

The space group appropriate for the specification of the structure of dhcp lanthanum belongs to space-group type $P6_3/mmc$ (No. 194). If the close-packed lanthanum atoms are chosen to occupy the Wyckoff positions $2c$ and $2a$, the octahedral interstitial sites O correspond to the Wyckoff position $4f$ with $z = \frac{1}{8}$, whereas the tetrahedral interstitial sites are

divided into two geometrically inequivalent crystallographic orbits: The tetrahedral sites of type T1 coincide with the Wyckoff position $4f$ with $z = \frac{1}{8} - \zeta$, and the sites of type T2 coincide with the Wyckoff position $4e$ with $z = \frac{1}{8} + \zeta$. Thereby, the centers of the interstitial sites are defined to be the positions with equal distance from the six or four coordinating lanthanum atoms; it holds that

$$\zeta = \frac{2}{3} \left(\frac{a}{c} \right)^2, \quad (1)$$

where a and c are the hexagonal lattice parameters.

The ccp structure is properly described on the basis of space-group type $Fm\bar{3}m$ (No. 225). The ccp lanthanum atoms are chosen to occupy the Wyckoff position $4a$, the octahedral interstitial sites correspond to the Wyckoff position $4b$, and the tetrahedral interstitial sites correspond to the Wyckoff position $8c$.

The conventional four-atom dhcp and ccp unit cells, however, are insufficient for the construction of models probing the diluted solution of hydrogen in lanthanum. As larger unit cells we have therefore used supercells and decentered supercells of the conventional unit cells. The Z -decentering of a supercell means that the basis vectors (and, as a consequence, the atomic positions in crystallographic coordinates) of the supercell undergo the transformation that leads from a Z -centered unit cell to the corresponding primitive unit cell. Thereby, Z stands for one of the letters symbolizing crystallographic centering (A , B , C , I , F , R). For the investigation of hydrogen arrangements in dhcp lanthanum, we have mainly made use of the $2 \times 2 \times 1$, the $3 \times 3 \times 1$, and the $4 \times 4 \times 1$ supercells of the conventional unit cell, which contain 16, 36, and 64 lanthanum atoms, respectively, and of the C -decentered $8 \times 4 \times 1$ supercell, which also contains 64 lanthanum atoms. Hydrogen arrangements in ccp lanthanum have been constructed mostly based on the $2 \times 2 \times 2$ and the $2 \times 2 \times 3$ supercells of the conventional unit cell with 32 and 48 lanthanum atoms, respectively, as well as on the I -decentered $2 \times 2 \times 2$ supercell with 16 lanthanum atoms. The C -decentered $8 \times 4 \times 1$ supercell of the hexagonal unit cell has orthorhombic axes; it can alternatively be considered as the $2 \times 2 \times 1$ supercell of the double orthohexagonal C cell²⁷ corresponding to the conventional dhcp unit cell. The 16-atom unit cell of ccp lanthanum has rhombohedral axes with the rhombohedral angle $\vartheta = \arccos(-1/3)$. The remaining above-mentioned model cells have hexagonal or orthogonal axes. We define that supercell formation and the possible subsequent decentering are not accompanied by a shift of the origin, i.e., the position vector (x, y, z) in crystallographic coordinates with respect to the conventional unit cell and the position vector $(x/m, y/n, z/p)$ in crystallographic coordinates with respect to the $m \times n \times p$ supercell correspond to the same Cartesian coordinates. All involved model cells have been optimized, and the total energies of the optimized structures serve as reference energies for the calculation of the hydrogenation energy E_h (see Sec. III B).

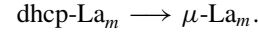
The formula $\mu\text{-La}_m\text{H}_n$, where $\mu = \text{dhcp, ccp}$, denotes a model structure that is defined by a unit cell made up of m lanthanum atoms in a dhcp or ccp arrangement and n hydrogen atoms occupying octahedral and/or tetrahedral interstitial sites. Analogously, the structures involving other rare-earth metals

are denoted by formulas corresponding to their unit cells. The total energy per unit cell of this structure is denoted by $E(\mu\text{-La}_m\text{H}_n)$. Where necessary, the coordination of a certain hydrogen atom, i.e., the type of the interstitial site occupied by the hydrogen atom, is specified by a superscript. For instance, the structure dhcp-La₃₆H^O results if one of the octahedral interstitial sites of dhcp-La₃₆, i.e., the $3 \times 3 \times 1$ supercell of the conventional unit cell of dhcp lanthanum, is occupied by a hydrogen atom.

B. Formation energetics

The formation of $\mu\text{-La}_m\text{H}_n$ is formally treated as the following three-step reaction sequence, which is formulated for the respective unit-cell size; the corresponding reaction energies are therefore calculated per unit cell.

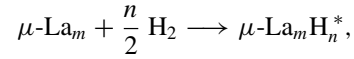
(1) Transform lanthanum from the dhcp phase to the phase corresponding to μ ,



The corresponding transformation energy $E_t(\mu\text{-La}_m)$ has not been calculated from the total energies of La_m cells but from the total energies of the conventional unit cells of dhcp and ccp lanthanum (see Sec. IV A),

$$E_t(\mu\text{-La}_m) = \begin{cases} 0, & \mu = \text{dhcp}, \\ m \times 3.19 \text{ meV}, & \mu = \text{ccp}. \end{cases} \quad (2)$$

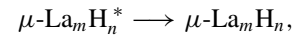
(2) Hydrogenate $\mu\text{-La}_m$, i.e., insert hydrogen atoms into interstitial sites leading to the unrelaxed, nonoptimized, structure $\mu\text{-La}_m\text{H}_n^*$,



which is associated with the hydrogenation energy

$$E_h(\mu\text{-La}_m\text{H}_n) = E(\mu\text{-La}_m\text{H}_n^*) - E(\mu\text{-La}_m) - \frac{n}{2} E(\text{H}_2). \quad (3)$$

(3) Perform structure optimization,



which is associated with the relaxation energy

$$E_r(\mu\text{-La}_m\text{H}_n) = E(\mu\text{-La}_m\text{H}_n) - E(\mu\text{-La}_m\text{H}_n^*). \quad (4)$$

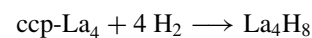
The formation energy is given as the sum of the transformation energy, the hydrogenation energy, and the relaxation energy,

$$E_f(\mu\text{-La}_m\text{H}_n) = E_t(\mu\text{-La}_m) + E_h(\mu\text{-La}_m\text{H}_n) + E_r(\mu\text{-La}_m\text{H}_n). \quad (5)$$

For the formation energy of stoichiometric lanthanum dihydride,

$$E_f(\text{La}_4\text{H}_8) = E(\text{La}_4\text{H}_8) - E(\text{dhcp-La}_4) - 4 E(\text{H}_2), \quad (6)$$

we have obtained $E_f(\text{La}_4\text{H}_8) = -7.996$ eV. $E(\text{La}_4\text{H}_8)$ is the total energy of fluorite-type lanthanum dihydride with the optimized lattice parameter $a = 5.649$ Å, which is in agreement with the experiment.²⁸ The reaction enthalpy corresponding to



has been determined calorimetrically at 917 K to be -7.928 ± 0.052 eV.²⁹ Combining the formation energy $E_f(\text{La}_4\text{H}_8)$ with the dhcp \rightarrow ccp transformation energy $E_t(\text{ccp-La}_4)$ given in equation (2), the energy difference corresponding to this reaction is calculated as -8.009 eV, which is in good agreement with the experimental value.

IV. RESULTS AND DISCUSSION

A. Elemental lanthanum

We have optimized the lattice parameters of dhcp, ccp, and bcc lanthanum under the constraint of symmetry conservation. In Table I, the results of these structure optimizations are compared to the corresponding experimental values. The total energies of the optimized structures have been calculated. The dhcp structure, i.e., the experimentally observed low-temperature structure, has turned out to be indeed the ground-state structure. The total energies of ccp and bcc lanthanum are stated in Table I relative to the total energy of dhcp lanthanum. In the course of structure optimizations without the constraint of point-symmetry conservation, i.e., opening all structural degrees of freedom of the space group $P1$, bcc lanthanum has transformed into ccp lanthanum via tetragonal distortion, whereas dhcp and ccp lanthanum are not affected.

For the optimized high-symmetry structures, the phonon-dispersion relations have been computed; they are displayed in Fig. 1. For dhcp and ccp lanthanum, no imaginary modes have been obtained; the energetically most favorable dhcp modification and the slightly less stable fcc modification therefore correspond to minima of the potential energy surface (PES), as opposed to the energetically unstable bcc structure, for which imaginary modes have been obtained, giving evidence that this structure does not correspond to a minimum of the PES. It is noted that the lowest phonon frequency of ccp lanthanum at the L point exhibits a strong sensitivity to the chosen \mathbf{k} mesh, which has been increased up to a $10 \times 10 \times 10$ Monkhorst-Pack mesh (0.06\AA^{-1} spacings) for the dispersion curves displayed in Fig. 1. Deviations from other calculated values, such as those given in Ref. 30, may originate from the \mathbf{k} -mesh dependence or from the treatment of the f electrons. The sensitivity to the \mathbf{k} mesh is related to the experimentally observed temperature-dependent phonon anomaly in Γ - L direction at (ζ, ζ, ζ) with $\zeta \approx 0.42$,³¹⁻³³ which was carefully analyzed in terms of Fermi-surface nesting features making use of *ab initio* techniques in Ref. 34.

TABLE I. Lattice parameters of the optimized lanthanum structures, the corresponding mean volumes v per atom, and the relative total energies E per atom. In parentheses, the experimental lattice parameters for samples at, or quenched to, room temperature are stated (see Ref. 2 and references therein).

Structure	c/a	$a/\text{\AA}$	$v/\text{\AA}^3$	E/meV
dhcp	3.206(3.225)	3.754(3.774)	36.710	0
ccp		5.263(5.303)	36.439	3.19
bcc		4.212(4.26)	37.352	128.34

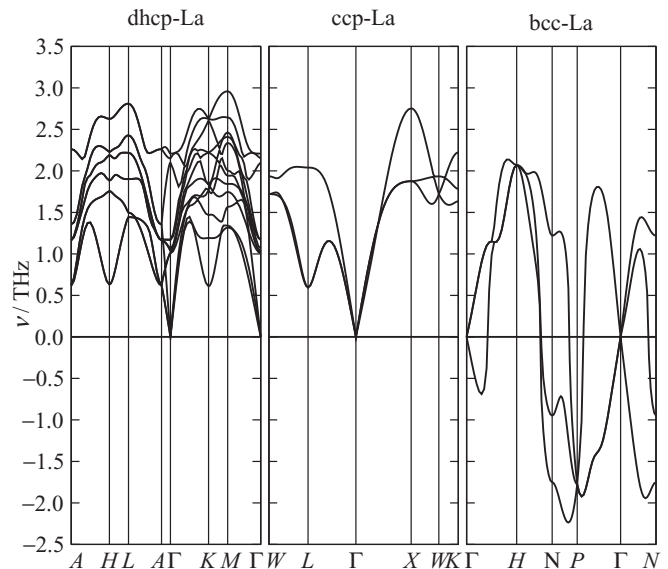


FIG. 1. The phonon-dispersion relations for dhcp, ccp, and bcc lanthanum. The Brillouin zones correspond to the Bravais lattices hP , cF , and cI , respectively. Imaginary frequencies are displayed as negative frequencies.

B. Spatially separated hydrogen atoms in dhcp and ccp lanthanum

As a first step in our study of the solid solution we have investigated spatially separated hydrogen atoms in dhcp and ccp lanthanum, the site preference (either for octahedrally or tetrahedrally coordinated interstitial sites), and the phase stability dhcp vs ccp as a function of the hydrogen concentration. To this end, we compare selected model structures, viz., dhcp- La_{16}H , ccp- La_{16}H , dhcp- La_{36}H , and ccp- La_{32}H , to one another. The optimizations of these $\mu\text{-La}_m\text{H}$ structures have always involved the lattice parameters and the atomic positions (i) confining the symmetry to the highest possible space-group symmetry \mathfrak{S} and (ii) without point-symmetry constraints, i.e., for space-group type $P1$ and a fixed number of atoms per unit cell. Comparing the high-symmetry results with the corresponding $P1$ results, only relatively small differences have been found; they are of the order of magnitude of mÅ or below for the shortest La-La and La-H distances and of the order of 10^{-4} eV or below for the total energies per unit cell. Therefore, further discussion is based on the relaxed high-symmetry structures. The optimized lattice parameters and the corresponding mean volumes per lanthanum atom as well as the formation energies, which are always exothermic, and their breakdown into hydrogenation and structure relaxation are given in Table II. For further $\mu\text{-La}_m\text{H}$ structures based on larger supercells, optimizations and total energy calculations have been performed. The formation energies calculated for dhcp- La_{64}H and ccp- La_{48}H have been used for the calculation of ordering energies in Sec. IV C.

The contribution of the structure optimization to the formation energies of the $\mu\text{-La}_m\text{H}$ structures is considerably larger if tetrahedrally coordinated hydrogen atoms are involved. The lowering of the total energy in the course of the optimization is more pronounced for dhcp- $\text{La}_m\text{H}^{\text{T}2}$ than for dhcp- $\text{La}_m\text{H}^{\text{T}1}$, which is connected to the elongation of the distance between

TABLE II. Structural and energetical characterization of selected μ -La_mH structures. The space groups of the highest possible symmetry \mathcal{G} , the lattice parameters of the relaxed structures, and the corresponding volumes per lanthanum atom v as well as the transformation energies E_t , the hydrogenation energies E_h , the relaxation energies E_r , and the formation energies E_f (according to the definitions in Sec. III B) are given. The axes are hexagonal for dhcp-La₃₆H and dhcp-La₁₆H, cubic for ccp-La₃₂H, and rhombohedral with the rhombohedral angle $\alpha = \arccos(-1/3)$ for ccp-La₁₆H.

Structure	\mathcal{G}	$a/\text{\AA}$	c/a	$v/\text{\AA}^3$	E_t/eV	E_h/eV	E_r/eV	E_f/eV
dhcp-La ₃₆ H ^O	$P3m1$	11.274	1.067	36.771	0	-0.743	-0.009	-0.752
dhcp-La ₃₆ H ^{T1}	$P3m1$	11.290	1.068	36.967	0	-0.633	-0.029	-0.662
dhcp-La ₃₆ H ^{T2}	$P3m1$	11.288	1.068	36.963	0	-0.646	-0.044	-0.690
dhcp-La ₁₆ H ^O	$P3m1$	7.533	1.597	36.963	0	-0.698	-0.006	-0.704
dhcp-La ₁₆ H ^{T1}	$P3m1$	7.562	1.598	37.399	0	-0.607	-0.027	-0.634
dhcp-La ₁₆ H ^{T2}	$P3m1$	7.545	1.608	37.374	0	-0.611	-0.066	-0.677
ccp-La ₃₂ H ^O	$Pm\bar{3}m$	10.516		36.338	0.102	-0.785	-0.001	-0.684
ccp-La ₃₂ H ^T	$P\bar{4}3m$	10.532		36.512	0.102	-0.604	-0.037	-0.539
ccp-La ₁₆ H ^O	$Im\bar{3}m$	9.124		36.541	0.051	-0.823	-0.000	-0.772
ccp-La ₁₆ H ^T	$Im\bar{3}m$	9.164		37.020	0.051	-0.645	-0.038	-0.632

the hydrogen atom and its second-nearest-neighbor lanthanum atom by 0.22 and 0.32 Å in the cases of dhcp-La₃₆H^{T2} and dhcp-La₁₆H^{T2}, respectively, as the major result of structure relaxation.³⁵

Relating the formation energies of structures with the same underlying lanthanum structure μ and with identical composition, i.e., structures that differ only with respect to the type of coordination of the hydrogen atom, it follows that hydrogen atoms are more tightly bonded in octahedral interstitial sites than in tetrahedral interstitial sites. The energetical difference between dhcp-La_mH^{T2} and dhcp-La_mH^O lies between about 0.03 and 0.06 eV for dhcp-La₁₆H, dhcp-La₃₆H, and also dhcp-La₆₄H; the occupation of a T1 site is always least favorable. For ccp lanthanum, the energetical difference between tetrahedral and octahedral coordination lies between 0.14 and 0.15 eV.

The zero-point energies have been calculated for those μ -La_mH structures for which phonon-dispersion relations without imaginary modes have been obtained, viz., dhcp-La₃₆H, ccp-La₃₂H, and ccp-La₁₆H (see below for the discussion of the phonon calculations). By comparison of the results for structures with the same underlying lanthanum structure μ and with identical composition it has turned out that the zero-point energy is lower by 0.050–0.056 eV per unit cell if the hydrogen atom occupies an octahedral interstitial site. Therefore, the zero-point vibration does not change the relative stability of the octahedral-site occupation in the case of the considered model structures.

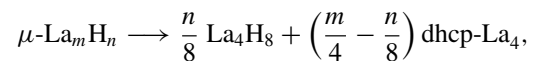
The hypothesis that hydrogen atoms preferentially occupy the octahedral interstitial sites of dhcp and ccp lanthanum is unorthodox in the context of the solid solution of hydrogen in a rare-earth metal. Direct experimental investigations of the structure of the metal-rich phases of the lanthanum-hydrogen system have never been performed as far as we know. Neutron powder-diffraction studies addressing this issue, however, are scheduled.³⁶ It is worthy of remark that positive muons, which can be seen as light hydrogen analogues, implanted in dhcp praseodymium are located at octahedral interstitial sites according to Knight-shift measurements³⁷ in contrast to hcp rare-earth metals in which hydrogen atoms and positive muons

both occupy tetrahedral sites. By analogy to the considerations for μ -La_mH structures, the site preference of hydrogen atoms in selected hcp rare-earth elements $R = \text{Sc, Y, Lu}$ has been tested on the basis of different supercells R_m of the conventional two-atom hcp unit cells (We have used the following supercells: $2 \times 2 \times 1$, $2 \times 2 \times 2$, $2 \times 2 \times 3$, and $3 \times 3 \times 2$, corresponding to $m = 8, 16, 24$, and 36). The hcp structure has interstitial sites of only two different types: octahedral (O) and tetrahedral (T). For the considered structures, the stabilization of $R_m\text{H}^T$ compared to $R_m\text{H}^O$ has been found to lie between 0.16 and 0.22 eV for scandium and between 0.25 and 0.30 eV for yttrium and lutetium.^{38,39}

The reaction energy

$$\begin{aligned} \Delta E &= \frac{n}{8} E_f(\text{La}_4\text{H}_8) - E_f(\mu\text{-La}_m\text{H}_n) \\ &= -1.000 \text{ eV} \times n - E_f(\mu\text{-La}_m\text{H}_n) \end{aligned} \quad (7)$$

corresponding to the segregation of $\mu\text{-La}_m\text{H}_n$ into pure dhcp lanthanum and stoichiometric lanthanum dihydride,



is exothermic for the investigated $\mu\text{-La}_m\text{H}$ structures (and the $\mu\text{-La}_m\text{H}_n$ structures discussed below). This can be seen as an indication that the hydrogen concentrations of the structures taken into account exceed the solubility limit of the solid solution.

The formation energies for $\mu\text{-La}_m\text{H}$ imply a change of the phase stability from dhcp for the lower hydrogen concentrations considered (comparing E_f for dhcp-La₃₆H^O and ccp-La₃₂H^O) to ccp for the higher hydrogen concentration considered (comparing E_f for dhcp-La₁₆H^O and ccp-La₁₆H^O).

Phonon-dispersion relations have been calculated for the optimized structures dhcp-La₃₆H, dhcp-La₁₆H, ccp-La₃₂H, and ccp-La₁₆H. All phonon modes of the three dhcp-La₃₆H structures, the two ccp-La₃₂H structures, and the two ccp-La₁₆H structures are real in contrast to the three dhcp-La₁₆H structures, for which imaginary modes have been obtained. In Fig. 2, the phonon-dispersion relations for ccp-La₁₆H^O

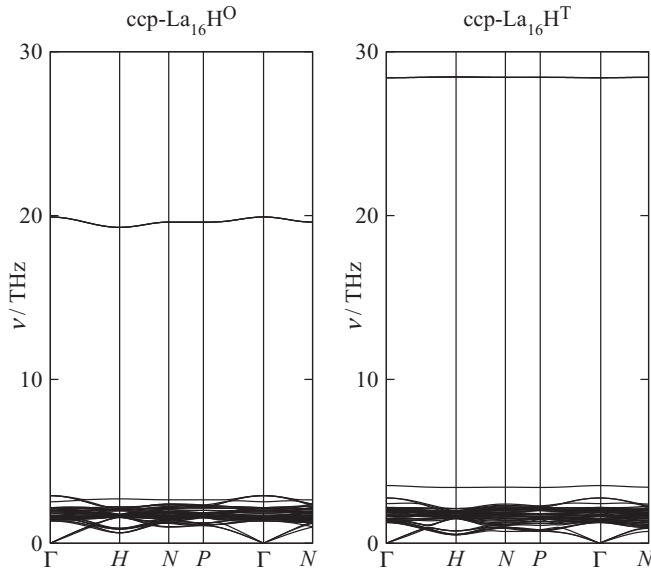


FIG. 2. Phonon-dispersion relations calculated for $\text{ccp-La}_{16}\text{H}^{\text{O}}$ and $\text{ccp-La}_{16}\text{H}^{\text{T}}$. The Brillouin zone corresponds to the body-centered cubic Bravais lattice.

and $\text{ccp-La}_{16}\text{H}^{\text{T}}$ are shown. The temperature-dependent free energies have been calculated from the total energies and the VDOS corresponding to the shown dispersion relations neglecting the contribution of the configurational entropy. Analogously, the free energies have been computed from the VDOS corresponding to the phonon-dispersion relations calculated for the structures $\text{ccp-La}_{32}\text{H}$ and $\text{dhcp-La}_{36}\text{H}$ (dispersion relations not shown) and their total energies. The relative free energies are plotted versus the temperature in Fig. 3. The contributions of the lattice vibrations to the free energy do not fundamentally influence the energetical preference for $\text{dhcp-La}_{36}\text{H}^{\text{O}}$ compared to $\text{dhcp-La}_{36}\text{H}$ with tetrahedrally coordinated hydrogen atoms in the temperature

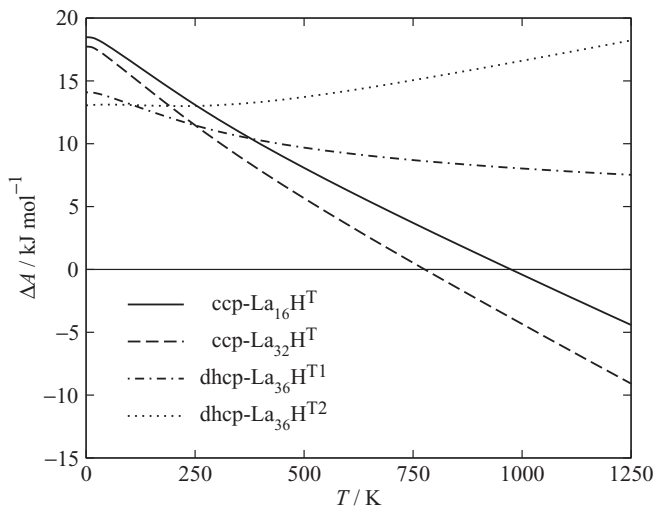


FIG. 3. Free energies of $\text{ccp-La}_m\text{H}^{\text{T}}$ relative to the free energies of $\text{ccp-La}_m\text{H}^{\text{O}}$ for $m = 16, 32$ and free energies of $\text{dhcp-La}_{36}\text{H}^{\text{T1}}$ and $\text{dhcp-La}_{36}\text{H}^{\text{T2}}$ relative to the free energy of $\text{dhcp-La}_{36}\text{H}^{\text{O}}$ derived from the calculated total energies and phonon data.

range relevant for dhcp lanthanum, i.e., within the existence range below about 580 K. In the case of the structures $\text{ccp-La}_{16}\text{H}$ and $\text{ccp-La}_{32}\text{H}$, on the contrary, the difference of the free energies changes sign at about 970 and 780 K, respectively, indicating that the energetical difference between octahedral and tetrahedral coordination of separated hydrogen atoms embedded in ccp lanthanum is reduced or even reversed at elevated temperature. This might be important for the interpretation of future experimental studies of the structure of the solid solution of hydrogen in (metastable) ccp lanthanum.

Interestingly, in very recent high-pressure experiments on $\text{LaH}_{2.3}$,⁴⁰ a phase separation has been observed and interpreted as a disproportionation reaction of the hyperstoichiometric dihydride into a trihydride and a correlated solid solution with octahedral site occupation. This could be an indication of favorable octahedral site occupation in ccp lanthanum, parallel to our analysis.

C. Hydrogen ordering

Whereas so far spatially separated hydrogen atoms were considered, this section focuses on the ordering tendencies of hydrogen atoms in dhcp and ccp lanthanum, i.e., the propensity of forming pairs, chains, and networks of pairs. In order to investigate hydrogen ordering, all possible structures of the series $\text{dhcp-La}_{16}\text{H}_2$, $\text{ccp-La}_{16}\text{H}_2$, and $\text{ccp-La}_{32}\text{H}_2$ have been considered; for $\text{dhcp-La}_{36}\text{H}_2$ and $\text{dhcp-La}_{64}\text{H}_2$, only selected model structures have been taken into account. The possible arrangements of two hydrogen atoms in a given unit cell $\mu\text{-La}_m$ have been figured out by determining the geometrically independent Wyckoff positions corresponding to the vacant interstitial sites of the $\mu\text{-La}_m\text{H}$ structures described on the basis of the respective most symmetrical space-group type \mathcal{G} (see Table II). Apart from $\mu\text{-La}_m\text{H}_2$ structures, several chainlike hydrogen configurations embedded in different unit cells $\mu\text{-La}_m$ have been investigated.

For a particular model structure $\mu\text{-La}_m\text{H}_n$, the hydrogen atoms within the unit cell are enumerated as H^1, H^2 , etc. The energetical effect due to the formation of hydrogen pairs and hydrogen chains embedded in dhcp and ccp lanthanum is specified by the ordering energy E_o , defined as follows:

$$E_o(\mu\text{-La}_m\text{H}_n) = E_h(\mu\text{-La}_m\text{H}_n) + E_r(\mu\text{-La}_m\text{H}_n) - \sum_{i=1}^n [E_h(\mu\text{-La}_m\text{H}^i) + E_r(\mu\text{-La}_m\text{H}^i)], \quad (8)$$

where the hydrogen atom in the unit cell of the structure designated as $\mu\text{-La}_m\text{H}^i$ occupies an interstitial site of the same type as the i th hydrogen atom in the unit cell of the $\mu\text{-La}_m\text{H}_n$ structure in question.

The structure optimizations of all considered $\mu\text{-La}_m\text{H}_n$ models have always included the lattice parameters and the atomic positions as relaxational degrees of freedom confining the symmetry to the respective most symmetrical space group.

1. Hydrogen ordering in dhcp lanthanum

Forty-five geometrically independent $\text{dhcp-La}_{16}\text{H}_2$ structures exist (7 $\text{La}_{16}\text{H}_2^{\text{O}}$, 22 $\text{La}_{16}\text{H}_2^{\text{T}}$, and 16 $\text{La}_{16}\text{H}^{\text{OHT}}$ structures). Among these structures, the five most favorable are

TABLE III. Structural and energetical characterization of selected model structures of the series dhcp-La₁₆H₂ and dhcp-La₃₆H₂. The types of the hydrogen atoms H^{*i*} corresponding to the types of the interstitial sites they occupy and their nonoptimized position vectors r_i in crystallographic coordinates as well as the hydrogenation energies E_h , the relaxation energies E_r , the formation energies E_f (according to the definitions in Sec. III B), and the ordering energies E_o [defined in Eq. (8)] are given.

Structure	H ¹	H ²	dhcp-La ₁₆ H ₂				dhcp-La ₃₆ H ₂							
			r_1	r_2	E_h/eV	E_r/eV	E_f/eV	E_o/eV	r_1	r_2	E_h/eV	E_r/eV	E_f/eV	E_o/eV
I	H ^O	H ^O	$\begin{pmatrix} 1/3 \\ 2/3 \\ 3/8 \end{pmatrix}$	$\begin{pmatrix} 2/3 \\ 1/3 \\ 5/8 \end{pmatrix}$	-1.604	-0.012	-1.616	-0.208	$\begin{pmatrix} 2/9 \\ 4/9 \\ 3/8 \end{pmatrix}$	$\begin{pmatrix} 4/9 \\ 2/9 \\ 5/8 \end{pmatrix}$	-1.525	-0.020	-1.545	-0.041
II	H ^{T2}	H ^O	$\begin{pmatrix} 0 \\ 0 \\ 1/8 + \zeta \end{pmatrix}$	$\begin{pmatrix} 1/3 \\ -1/3 \\ 3/8 \end{pmatrix}$	-1.598	-0.075	-1.673	-0.292	$\begin{pmatrix} 0 \\ 0 \\ 1/8 + \zeta \end{pmatrix}$	$\begin{pmatrix} 2/9 \\ -2/9 \\ 3/8 \end{pmatrix}$	-1.462	-0.054	-1.516	-0.074
III	H ^{T1}	H ^{T1}	$\begin{pmatrix} 1/3 \\ 2/3 \\ 5/8 - \zeta \end{pmatrix}$	$\begin{pmatrix} 2/3 \\ 1/3 \\ 3/8 + \zeta \end{pmatrix}$	-1.626	-0.061	-1.687	-0.419	$\begin{pmatrix} 2/9 \\ 4/9 \\ 5/8 - \zeta \end{pmatrix}$	$\begin{pmatrix} 4/9 \\ 2/9 \\ 3/8 + \zeta \end{pmatrix}$	-1.380	-0.061	-1.441	-0.117
IV	H ^{T1}	H ^{T1}	$\begin{pmatrix} 1/3 \\ 2/3 \\ 5/8 - \zeta \end{pmatrix}$	$\begin{pmatrix} 1/3 \\ 2/3 \\ 7/8 + \zeta \end{pmatrix}$	-1.374	-0.074	-1.448	-0.180	$\begin{pmatrix} 2/9 \\ 4/9 \\ 5/8 - \zeta \end{pmatrix}$	$\begin{pmatrix} 2/9 \\ 4/9 \\ 7/8 + \zeta \end{pmatrix}$	-1.410	-0.078	-1.488	-0.162
V	H ^{T2}	H ^{T2}	$\begin{pmatrix} 0 \\ 0 \\ 3/8 - \zeta \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \\ 5/8 + \zeta \end{pmatrix}$	-1.372	-0.069	-1.441	-0.087	$\begin{pmatrix} 0 \\ 0 \\ 3/8 - \zeta \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \\ 5/8 + \zeta \end{pmatrix}$	-1.426	-0.063	-1.489	-0.109
VI	H ^{T1}	H ^{T2}	$\begin{pmatrix} -1/3 \\ 1/3 \\ 1/8 - \zeta \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \\ 1/8 + \zeta \end{pmatrix}$	-1.221	-0.097	-1.318	-0.007	$\begin{pmatrix} -2/9 \\ 2/9 \\ 1/8 - \zeta \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \\ 1/8 + \zeta \end{pmatrix}$	-1.277	-0.081	-1.358	-0.006
VII	H ^{T2}	H ^{T2}	$\begin{pmatrix} 0 \\ 0 \\ 1/8 + \zeta \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \\ 3/8 - \zeta \end{pmatrix}$	-0.841	-0.451	-1.292	+0.062	$\begin{pmatrix} 0 \\ 0 \\ 1/8 + \zeta \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \\ 3/8 - \zeta \end{pmatrix}$	-0.876	-0.435	-1.311	+0.069

those for which the two hydrogen atoms are collinearly (or almost collinearly) bonded to a central lanthanum atom. These structures, I–V, are characterized in Table III with respect to the hydrogen positions, formation energies, and ordering energies. The ordering energies obtained for them are stronger exothermic than for all other La₁₆H₂ structures. In other words, stabilization is achieved if the coordination polyhedra of the hydrogen atoms embedded in the unit cell are linked via a common vertex so that a linear (or an almost linear) H-La-H arrangement results. Such a structural element is hereafter referred to as a hydrogen pair. It can be made up of two octahedrally coordinated hydrogen atoms (I), two tetrahedrally coordinated hydrogen atoms (III–V), or two hydrogen atoms with different coordination numbers (II). In the latter case only, it is not strictly linear; the angle between the La-H bonds in the optimized structure II is 169°, which is still closer to 180° than for any other dhcp-La₁₆H₂ structure with one octahedrally and one tetrahedrally coordinated hydrogen atom bonded to the same lanthanum atom. The stabilization due to the formation of H-La-H elements is not an implication of the structure optimization; it is clearly revealed on the basis of the hydrogenation energies of the 45 dhcp-La₁₆H₂ structures. The hydrogenation energies and the relaxation energies are given in Table III.

For the solid-solution phases of hydrogen in several rare-earth metals with hcp structure, hydrogen pairs in the sense of linear arrangements parallel to the *c* axis consisting of two tetrahedrally coordinated hydrogen atoms collinearly bonded to a central metal atom are observed as basic structural element of chainlike hydrogen arrangements (see Ref. 10 and references therein). In a matrix of hexagonal close-packed metal atoms *M*, either two tetrahedrally coordinated hydrogen atoms or a tetrahedrally coordinated hydrogen atom together with an octahedrally coordinated hydrogen atom can form a hydrogen pair in the sense of a H-*M*-H arrangement with collinear or almost collinear H-*M* bonds. The hcp structure therefore offers less topological degrees of freedom for the generation of hydrogen pairs than the dhcp structure. The investigation of all possible structures obtained by placing two hydrogen atoms at interstitial sites within the 2 × 2 × 3 supercells of the conventional unit cells of the hcp rare-earth metals scandium, yttrium, and lutetium shows that the pairing of hydrogen atoms interstitially bonded in these rare-earth metals chosen for comparison is stabilizing and leads to an enhancement of the energetical preference for the occupation of tetrahedral interstitial sites.^{38,39}

The ordering energies of the five energetically most favorable dhcp-La₁₆H₂ structures cannot be directly compared

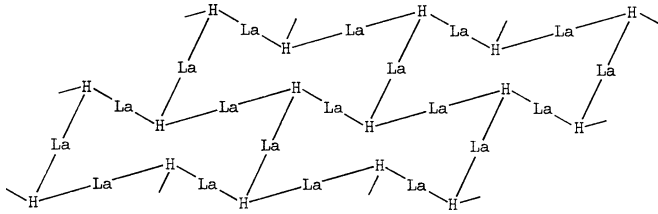


FIG. 4. Schematic semiperspective representation (analogous to the usual depiction of cyclohexane chairs) of the infinitely extended networks of linked H-La-H elements formed as a result of the translation symmetry in the case of structures I, II, and III of the dhcp-La₁₆H₂ series.

to each other because the translation symmetry partially leads to a tripling of the number of H-La-H arrangements per unit cell, which can be concluded from the following argument: the shortest distance vector between the hydrogen atoms H¹ and H² of a particular dhcp-La₁₆H₂ structure in crystallographic coordinates is denoted by $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$. For structures I, II, and III, it holds that

$$\tilde{\mathbf{r}} = \mathcal{C}_3 \mathbf{r} = \begin{pmatrix} 0 & -1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \mathbf{r} = \mathbf{r} + \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad (9)$$

and

$$\tilde{\tilde{\mathbf{r}}} = \mathcal{C}_3 \tilde{\mathbf{r}} = \mathcal{C}_3^2 \mathbf{r} = \begin{pmatrix} -1 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \mathbf{r} = \mathbf{r} - \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad (10)$$

where \mathcal{C}_3 stands for the threefold rotation through H¹. This is readily seen taking the positions of the hydrogen atoms from Table III. Because of the adopted symmetry conservation, this argument is also valid for the optimized structures in question. The positions of the lanthanum atoms and all translationally equivalent H¹ atoms are invariant under this rotation because the symmetry of the three dhcp-La₁₆H structures is expressed by space groups of the type $P3m1$. It therefore follows from (9) and (10) that the translation symmetry leads to a tripling of the number of H-La-H elements per unit cell of structures I, II, and III associated with the hydrogen-hydrogen distance vectors \mathbf{r} , $\tilde{\mathbf{r}}$, and $\tilde{\tilde{\mathbf{r}}}$. The triplicated H-La-H elements are directly linked together and are arranged in the form of six-membered rings in chair conformation, which are condensed to infinitely extended networks sketched in Fig. 4. In the case of the other structures with hydrogen pairs, viz., structures IV and V, the number of H-La-H elements per unit cell is not increased by the translation symmetry.

The ordering energy of the network-forming structure dhcp-La₁₆H₂ III is a multiple of the ordering energies calculated for structures IV and V. This fact is interpreted as an extra stabilization due to the increased number of favorable H-La-H arrangements per unit cell in view of the ordering energies calculated for hydrogen pairs in larger unit cells (see the next paragraph).

We have abstained from the computationally demanding systematical investigation of all possible structures resulting from the insertion of two hydrogen atoms into the $3 \times 3 \times 1$ supercell dhcp-La₃₆ or even larger unit cells. In order to

evaluate the ordering energy for isolated H-La-H elements, however, the five hydrogen arrangements corresponding to structures I–V of the dhcp-La₁₆H₂ series have been transferred to the dhcp-La₃₆ cell; i.e., the particular H-La-H configurations have been embedded in a larger unit cell for which the network formation on account of the translation symmetry is excluded in contrast to dhcp-La₁₆ so that the comparison of ordering energies becomes feasible. In the larger unit cell, the pairs are isolated in the sense that the constituent atoms of one H-La-H element is not part of another one. The hydrogen positions as well as the calculated formation energies together with the contributions from hydrogenation and relaxation and the ordering energies are given in Table III. It is noticed that the lowering of the total energy due to hydrogen ordering is drastically smaller for the dhcp-La₃₆H₂ structures I–III than for the corresponding dhcp-La₁₆H₂ models, where the superior stabilization of the latter has been attributed to the formation of extended networks above. The sequence of the ordering energies of the dhcp-La₃₆H₂ structures I–V implies that the energetic impact due to the formation of isolated hydrogen pairs is larger for tetrahedrally coordinated hydrogen atoms. Hence, hydrogen pairing partially neutralizes the preference for the occupation of octahedral interstitial sites, which is observed for spatially separated hydrogen atoms. This is clearly seen on the basis of the hydrogenation energies and cannot be attributed to the generally larger contribution of the relaxation energy in the case of tetrahedral coordination. The contribution of the relaxation energy to the formation energy, which is always larger if tetrahedrally coordinated hydrogen atoms are involved, does not change the energetical sequence of the stabilized structures I–V. The formation of extended networks and, as discussed below, the formation of extended chains even lead to a reversal of the site preference.

In Fig. 5, the DOS calculated for elemental dhcp lanthanum, for the dhcp-La₃₆H structures, and for structures I–VI of the dhcp-La₃₆H₂ series are shown. A common feature of structures I–V is a distinct splitting of the DOS in the energy range of the hydrogen *s* bands into two separate peaks in contrast to all other dhcp-La₃₆H₂ structures for which the DOS has been calculated. This is demonstrated for structure VI, which has been selected for comparison because the shortest distance between the tetrahedrally coordinated hydrogen atoms of this structure (see Table III) is similar to the length of the H-La-H element of structures III, IV, and V, but no lanthanum atom is centered between the hydrogen atoms. The width of the gap between the separated hydrogen *s* bands is about 0.4 eV for structure I, about 0.5 eV for structure II, and between 0.7 and 0.8 eV for structures III–V. The site-projected and *l*-projected DOS have been calculated for dhcp-La₃₆H and the dhcp-La₃₆H₂ structures I–V. Only the hydrogen *s* states and states of the lanthanum atoms making up the first coordination shell of the hydrogen atoms contribute significantly to the total DOS in the energy range of the hydrogen *s* bands between –5 and –4 eV measured relative to the Fermi energy. The lanthanum atoms centered between the pair-forming hydrogen atoms of structures I–V contribute to the lower-energy peak in the range between –5 and –4 eV exclusively with their *s* and *d* states and to the higher-energy peak predominantly with their *p* states and to a smaller extent with their *f* states (in the case of structure II *d* and small *s* contributions are

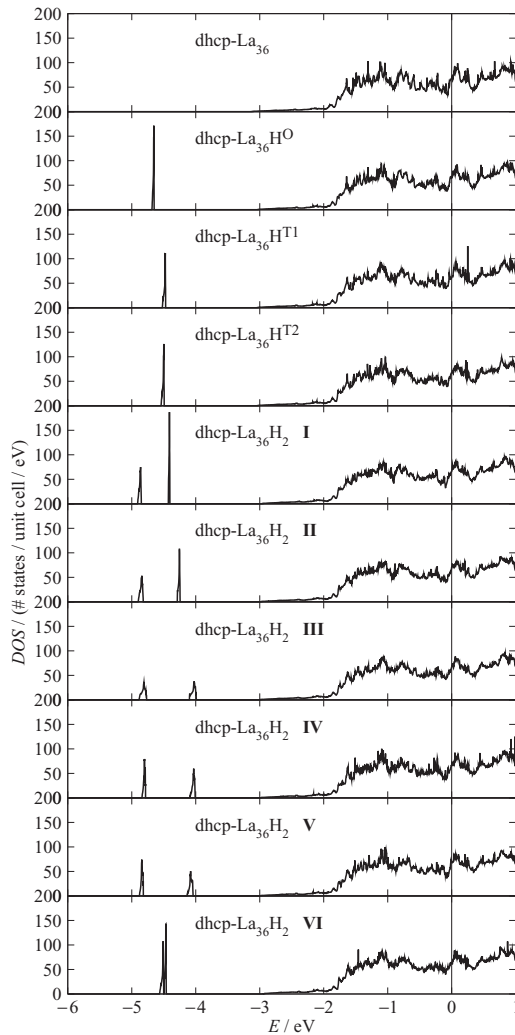


FIG. 5. DOS for elemental lanthanum (36-atom supercell), for the optimized structures dhcp-La₃₆H, and for structures I–VI of the dhcp-La₃₆H₂ series. The energy is measured relative to the Fermi energy.

also found). The hybridization patterns of these lanthanum atoms display a splitting in states that are gerade (*s* and *d*) or ungerade (*p* and *f*) with respect to the symmetry of an isolated linear H-La-H unit. The contribution of the remaining lanthanum atoms directly bonded to hydrogen to both peaks in the energy range between -5 and -4 eV has *s*, *p*, *d*, and *f* characters, where the *d* character dominates. An analogous bonding mechanism is observed for hydrogen pairs in the hcp metals scandium and yttrium¹¹ as well as lutetium.^{38,39}

Remarkably, highly destabilized nonoptimized structures with a hydrogen-hydrogen distance of 1.50 Å result if the coordination tetrahedra of two hydrogen atoms share a common face (structure VII of Table III). The main impact of the optimization on structure VII of the series dhcp-La₁₆H₂ and dhcp-La₃₆H₂ is a shift of the hydrogen atoms H^I and H^{II} in $-c$ and $+c$ directions, such that the hydrogen-hydrogen distances are 2.05 Å and 2.07 Å, respectively, in the relaxed structures. This structural change is accompanied by a marked lowering of the total energy, so that the differences between the formation energies of structures VII and VI are smaller than

the differences between the respective hydrogenation energies by an order of magnitude. This behavior is in agreement with the Switendick criterion,⁴¹ which implies a repulsive interaction between interstitially bonded hydrogen atoms in metals leading to a minimum hydrogen-hydrogen distance of approximately 2.1 Å.

Translationally periodic chainlike arrangements of hydrogen atoms interstitially bonded in dhcp lanthanum have been constructed on the basis of the supercells dhcp-La₆₄ with hexagonal and orthorhombic axes. These structures (VIII–XVI) are defined with respect to the positions of the hydrogen atoms in Table IV and sketched in Fig. 6. All chains taken into account consist of four hydrogen atoms per unit cell that form hydrogen pairs H-La-H directly linked together so that every hydrogen atom is part of two pairs. Thus, the unit cells of structures VIII–XVI contain eight La-H bonds making up the chains. The chains differ in regard to their conformation, their orientation with respect to the lattice vectors, and the coordination type of the individual hydrogen atoms. The formation energies and the ordering energies are given in Table IV. The stabilizing effect of ordering is larger if tetrahedrally coordinated hydrogen atoms participate in chain formation in accordance with the observations for pairs in dhcp-La₃₆H₂. On the basis of the ordering energies calculated for dhcp-La₆₄H₄ and the pair-forming dhcp-La₆₄H₂ structures, it can be approximated that hydrogen ordering as represented by structures VIII–XVI leads to a lowering of the total energy by about 0.02 or 0.06 eV per La-H bond being part of the chain, depending on whether the hydrogen atom in question occupies an octahedral or a tetrahedral interstitial site. This again shows that hydrogen ordering can oppose the preference for octahedral coordination observed for unpaired hydrogen atoms in dhcp-La_{*m*}H. Actually, this site preference is found to be reversed as a consequence of the formation of chains of H^{T1} atoms aligned parallel to the *c* axis. The optimized structures XI, XV, and XVI are the stablest members of the dhcp-La₆₄H₄ series.

2. Hydrogen ordering in ccp lanthanum

The investigation of the 19 independent ccp-La₃₂H₂ models (5 La₃₂H₂^O, 10 La₃₂H₂^T, and 4 La₃₂H₂^{OHT} structures) has shown that the formation of linear pairs of hydrogen atoms bonded to a central lanthanum atom is energetically favored, analogous to the situation of hydrogen atoms interstitially bonded in dhcp lanthanum. Two realizations of such pairs exist that are made up of two either tetrahedrally or octahedrally coordinated hydrogen atoms. Pair formation is excluded if the two hydrogen atoms have different coordination numbers. For the unit cell ccp-La₃₂ with a lanthanum atom at the position (0, 0, 0), it is possible to choose the positions occupied by the paired hydrogen atoms to be $\pm(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$ in the case of H^T atoms and $\pm(0, 0, \frac{1}{4})$ in the case of H^O atoms. Because also $(0, 0, \frac{1}{2})$ corresponds to a lanthanum position, translation-equivalent pairs of hydrogen atoms at octahedral sites are directly connected to each other so that the favorable ccp-La₃₂H₂^O model structure does in fact not represent an isolated pair but an infinitely extended chain of La-H bonds corresponding to two linear H^O-La-H^O elements per unit cell, whereas two H^T atoms can only form a single pair in the ccp-La₃₂ unit cell.

TABLE IV. Structural and energetical characterization of the constructed dhcp-La₆₄H₄ structures with chainlike hydrogen arrangements based on the hexagonal 4 × 4 × 1 cell and on the orthorhombic C-decentered 8 × 4 × 1 cell. The types of the hydrogen atoms Hⁱ according to the types of the interstitial sites they occupy and their nonoptimized position vectors r_i in crystallographic coordinates as well as the hydrogenation energy E_h , the relaxation energy E_r , and the formation energy E_f (according to the definitions in Sec. III B) and the ordering energy per hydrogen atom E_o [defined in Eq. (8)] are given.

Structure	H ¹	H ²	H ³	H ⁴	r_1	r_2	r_3	r_4	E_h/eV	E_r/eV	E_f/eV	E_o/eV
Structures based on hexagonal unit cell												
VIII	H ^O	H ^O	H ^O	H ^O	$\begin{pmatrix} 7/12 \\ 1/6 \\ 5/8 \end{pmatrix}$	$\begin{pmatrix} 5/12 \\ 1/3 \\ 3/8 \end{pmatrix}$	$\begin{pmatrix} 7/12 \\ 2/3 \\ 5/8 \end{pmatrix}$	$\begin{pmatrix} 5/12 \\ 5/6 \\ 3/8 \end{pmatrix}$	-3.079	-0.039	-3.118	-0.160
IX	H ^{T2}	H ^O	H ^{T2}	H ^O	$\begin{pmatrix} 1/2 \\ 0 \\ 1/8 + \zeta \end{pmatrix}$	$\begin{pmatrix} 2/3 \\ 1/3 \\ 3/8 \end{pmatrix}$	$\begin{pmatrix} 1/2 \\ 1/2 \\ 1/8 + \zeta \end{pmatrix}$	$\begin{pmatrix} 2/3 \\ 5/6 \\ 3/8 \end{pmatrix}$	-3.003	-0.146	-3.149	-0.324
X	H ^{T1}	H ^{T1}	H ^{T1}	H ^{T1}	$\begin{pmatrix} 7/12 \\ 1/6 \\ 3/8 + \zeta \end{pmatrix}$	$\begin{pmatrix} 5/12 \\ 1/3 \\ 5/8 - \zeta \end{pmatrix}$	$\begin{pmatrix} 7/12 \\ 2/3 \\ 3/8 + \zeta \end{pmatrix}$	$\begin{pmatrix} 5/12 \\ 5/6 \\ 5/8 - \zeta \end{pmatrix}$	-2.948	-0.187	-3.135	-0.478
XI	H ^{T1}	H ^{T1}	H ^{T1}	H ^{T1}	$\begin{pmatrix} 7/12 \\ 5/12 \\ 1/8 - \zeta \end{pmatrix}$	$\begin{pmatrix} 7/12 \\ 5/12 \\ 3/8 + \zeta \end{pmatrix}$	$\begin{pmatrix} 5/12 \\ 7/12 \\ 5/8 - \zeta \end{pmatrix}$	$\begin{pmatrix} 5/12 \\ 7/12 \\ 7/8 + \zeta \end{pmatrix}$	-2.965	-0.210	-3.175	-0.518
Structures based on orthorhombic unit cell												
XII	H ^O	H ^O	H ^O	H ^O	$\begin{pmatrix} 5/8 \\ 1/12 \\ 5/8 \end{pmatrix}$	$\begin{pmatrix} 5/8 \\ 5/12 \\ 3/8 \end{pmatrix}$	$\begin{pmatrix} 3/8 \\ 7/12 \\ 5/8 \end{pmatrix}$	$\begin{pmatrix} 3/8 \\ 11/12 \\ 3/8 \end{pmatrix}$	-3.094	-0.036	-3.130	-0.153
XIII	H ^{T2}	H ^O	H ^{T2}	H ^O	$\begin{pmatrix} 1/2 \\ 0 \\ 1/8 + \zeta \end{pmatrix}$	$\begin{pmatrix} 1/4 \\ 1/6 \\ 3/8 \end{pmatrix}$	$\begin{pmatrix} 1/4 \\ 1/2 \\ 1/8 + \zeta \end{pmatrix}$	$\begin{pmatrix} 1/2 \\ 2/3 \\ 3/8 \end{pmatrix}$	-3.014	-0.156	-3.170	-0.312
XIV	H ^{T1}	H ^{T1}	H ^{T1}	H ^{T1}	$\begin{pmatrix} 5/8 \\ 1/12 \\ 3/8 + \zeta \end{pmatrix}$	$\begin{pmatrix} 5/8 \\ 5/12 \\ 5/8 - \zeta \end{pmatrix}$	$\begin{pmatrix} 3/8 \\ 7/12 \\ 3/8 + \zeta \end{pmatrix}$	$\begin{pmatrix} 3/8 \\ 11/12 \\ 5/8 - \zeta \end{pmatrix}$	-2.954	-0.198	-3.152	-0.473
XV	H ^{T1}	H ^{T1}	H ^{T1}	H ^{T1}	$\begin{pmatrix} 0 \\ 1/3 \\ 1/8 - \zeta \end{pmatrix}$	$\begin{pmatrix} 0 \\ 1/3 \\ 3/8 + \zeta \end{pmatrix}$	$\begin{pmatrix} 0 \\ 2/3 \\ 5/8 - \zeta \end{pmatrix}$	$\begin{pmatrix} 0 \\ 2/3 \\ 7/8 + \zeta \end{pmatrix}$	-2.978	-0.215	-3.193	-0.514
XVI	H ^{T1}	H ^{T1}	H ^{T1}	H ^{T1}	$\begin{pmatrix} 1/2 \\ 1/3 \\ 1/8 - \zeta \end{pmatrix}$	$\begin{pmatrix} 1/2 \\ 1/3 \\ 3/8 + \zeta \end{pmatrix}$	$\begin{pmatrix} 3/4 \\ 1/6 \\ 5/8 - \zeta \end{pmatrix}$	$\begin{pmatrix} 3/4 \\ 1/6 \\ 7/8 + \zeta \end{pmatrix}$	-2.992	-0.210	-3.202	-0.523

In order to evaluate the ordering energies for single pairs and chains, the pair of octahedrally coordinated hydrogen atoms has been transferred from the ccp-La₃₂ cell to the ccp-La₄₈ cell in two different ways: either perpendicular or parallel to the c axis. The resulting ccp-La₄₈H₂^O structures XVII and XVIII as well as structure XIX with a single pair of hydrogen atoms occupying tetrahedral sites are shown in Fig. 7. Furthermore, the ccp-La₄₈ cell has been used for the construction of disconnected and infinitely extended chains consisting of linked pairs of four tetrahedrally coordinated hydrogen atoms. These chains are realized in structures XX–XXIII, which are also depicted in Fig. 7. In Table V, the formation energies (split into the contributions from transformation, hydrogenation, and structure relaxation) and the ordering energies obtained for structures XVII–XXIII are given. Along with chain formation

and therefore an increased number of H^O-La-H^O units, the lowering of the total energy as a consequence of hydrogen ordering favors structure XVII compared to structure XVIII. A similar behavior has been observed for chains consisting of four tetrahedrally coordinated hydrogen atoms inserted into the ccp-La₄₈ cell, which form three or four concatenated H-La-H units in the form of zigzag-shaped chains (XX and XXI) or helicoidal chains (XXII and XXIII). Structures XX and XXI differ from each other with respect to the orientation of the hydrogen quadruple relative to the tetragonal lattice vectors corresponding to the unit cell ccp-La₄₈. The same holds for structures XXII and XXIII. Whereas, by virtue of the translation symmetry, infinitely extended chains of eight linked La-H bonds per unit cell are present in structures XX and XXII, the unit cells of structures XXI and XXIII contain

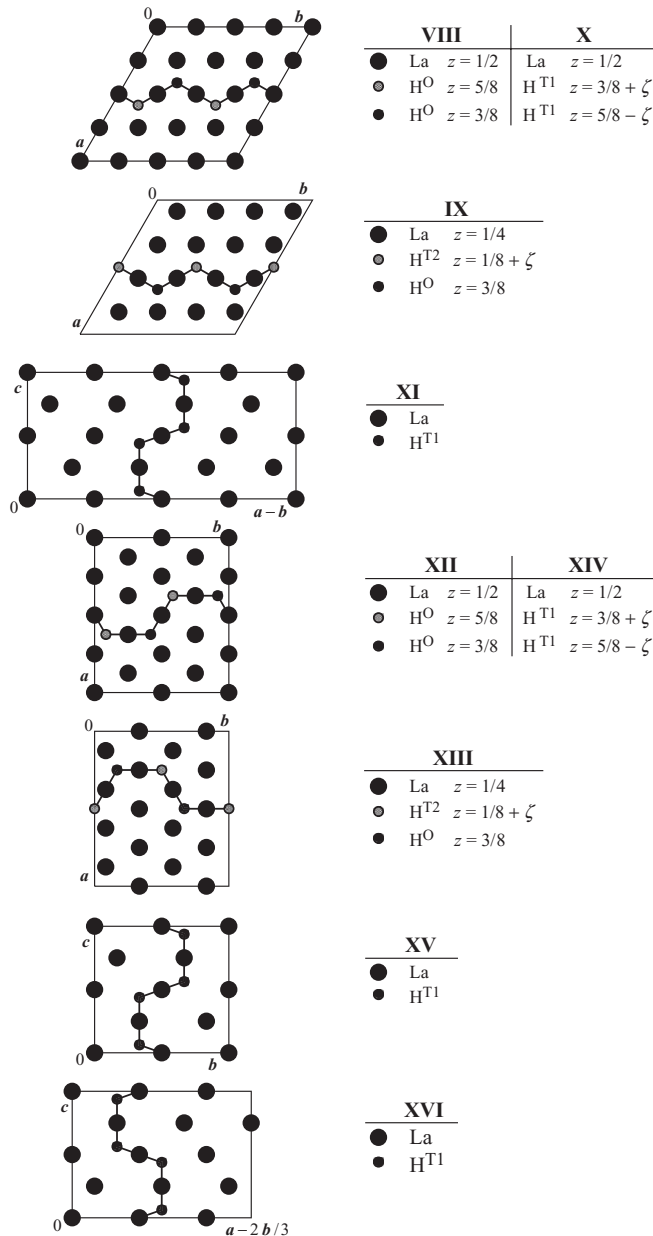


FIG. 6. The dhcp-La₆₄H₄ chain models VIII–XVI according to Table IV. The images for structures VIII–X and XII–XIV show the position of the lanthanum atoms in planes perpendicular to the *c* axis and the projections of the positions of the hydrogen atoms onto these planes. For structures XI, XV, and XVI the positions of the atoms in planes (110) and (100) and a plane parallel to the (230) plane, respectively, are shown. Each image represents the intersection of the selected net plane and the unit cell. (The vectors corresponding to the sides of the maps and the origin 0 or its projection are indicated.)

only six La-H bonds along the chains. It is clearly revealed on the basis of the stated formation energies that structures XX and XXII are the preferred ccp-La₄₈H₄¹ structures.

Comparing the ordering energies stated in Table V for the structures with linear H-La-H arrangements and chains consisting of such elements, it follows that the stabilization due to the formation of hydrogen pairs and hydrogen chains is more effective for hydrogen atoms that are tetrahedrally coordinated by ccp lanthanum atoms. In agreement with the results

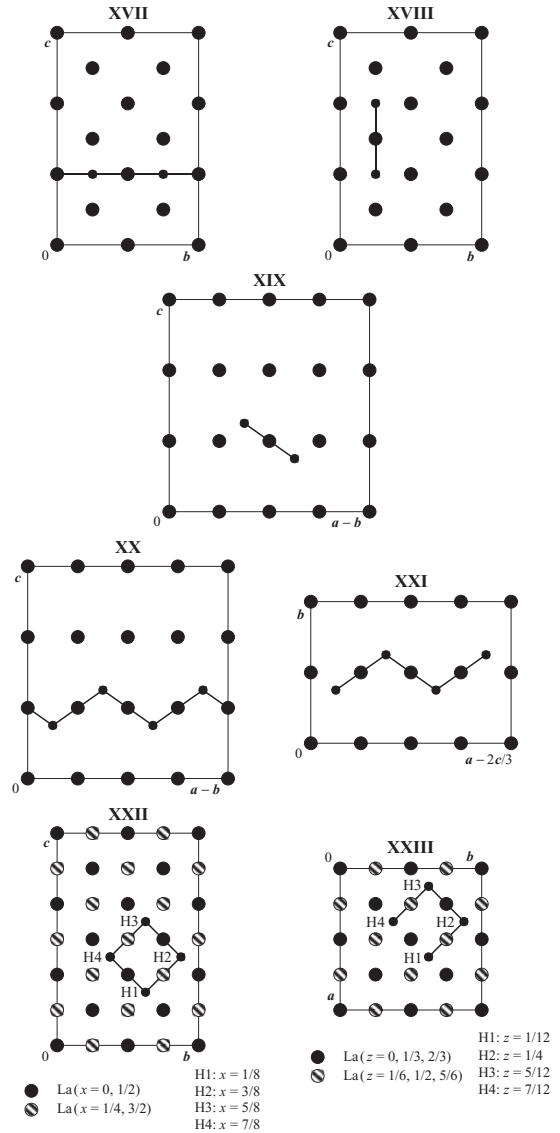


FIG. 7. The considered ccp-La₄₈H_{*n*} structures. The positions of the lanthanum atoms (solid circles) and the hydrogen atoms (open circles) of structures XVII and XVIII in the (100) plane, the atomic positions of structures XIX and XX in the (110) plane, and the atomic positions of structure XXI in a plane parallel to the (203) plane. The atomic positions of structures XXII and XXIII are projected onto the (100) and the (001) plane, respectively. Each illustration corresponds to the intersection of the respective net plane or projection and the unit cell. (The vectors corresponding to the sides of the maps and the origin 0 or its projection are indicated.) Apart from the representation of structure XXI, all images show two-dimensional translation periods.

obtained for dhcp-La₃₆H₂ and dhcp-La₆₄H₄ discussed above, the ordering energy per La-H bond as part of a H-La-H unit is about -0.02 eV or between -0.06 and -0.05 eV, depending on the coordination numbers of the involved hydrogen atoms. Different from the situation of hydrogen atoms in a matrix of dhcp lanthanum, however, the preference for the occupation of octahedral interstitial sites is not reversed by virtue of chain formation because of the larger energetical difference between octahedral and tetrahedral coordination of unpaired hydrogen atoms in ccp lanthanum.

TABLE V. The transformation energy E_t , hydrogenation energy E_h , relaxation energy E_r , and formation energy E_f (according to the definitions in Sec. III B) as well as the ordering energy per hydrogen atom E_o [defined in Eq. (8)] for the considered ccp-La₄₈H_{*n*} structures with linear H-La-H arrangements.

Structure	<i>n</i>	E_t /eV	E_h /eV	E_r /eV	E_f /eV	E_o /eV
XVII	2	0.153	-1.662	-0.008	-1.517	-0.088
XVIII	2	0.153	-1.607	-0.005	-1.459	-0.030
XIX	2	0.153	-1.307	-0.086	-1.240	-0.116
XX	4	0.153	-2.764	-0.200	-2.811	-0.410
XXI	4	0.153	-2.710	-0.194	-2.751	-0.350
XXII	4	0.153	-2.790	-0.213	-2.850	-0.449
XXIII	4	0.153	-2.703	-0.194	-2.744	-0.343

It is noteworthy that the comparison of model structures for hypostoichiometric lanthanum dihydride derived from the $2 \times 2 \times 2$ supercell of the conventional fluorite-type unit cell (La₃₂H₆₄) has shown that the linear arrangement of two vacant tetrahedral interstitial sites around a central lanthanum atom is stabilized by about 0.3 eV with respect to the other arrangements possible for this unit cell and with respect to single vacancies. In other words, those vacancy pairs in the dihydride are energetically favorable that are geometrically equivalent to the pairs of tetrahedrally coordinated hydrogen atoms favored in the solid-solution phase. The fluorite-type structure of lanthanum dihydride can be considered as a network of cross-linked La-H bonds, in which every hydrogen atom is part of four H-La-H elements. Consequently, the withdrawal of two hydrogen atoms from lanthanum dihydride leads to a reduction of the number of H-La-H elements by 8, unless the arrangement of the two introduced hydrogen vacancies is geometrically equivalent to the favorable hydrogen pair. (Then, the number of H-La-H elements is reduced by only 7.) In this sense, the formation of vacancy pairs in hypostoichiometric lanthanum dihydride is complementary to the formation of hydrogen pairs in the solid solution of hydrogen in ccp lanthanum.

V. CONCLUSIONS

Total energy calculations for various structurally optimized models probing the diluted solid solution of hydrogen in lanthanum suggest that hydrogen atoms occupying spatially separated interstitial sites of dhcp and ccp lanthanum show an energetical preference for octahedral coordination at zero temperature. This is a completely unexpected result for the solid solution of hydrogen in a rare-earth metal, even though

direct experimental indications are currently not available, to our knowledge.

The temperature-dependent free energies calculated for selected model structures indicate that the energetical preference for the occupation of octahedral interstitial sites is reduced or reversed at higher temperature in the case of ccp lanthanum, contrary to the situation of hydrogen in dhcp lanthanum.

It has been found that ordering characterized by the formation of structural elements that consist of two hydrogen atoms that occupy adjacent interstitial sites of dhcp and ccp lanthanum and that are collinearly bonded to a central lanthanum atom (referred to as hydrogen pairs) leads to a lowering of the energy compared to the case of unpaired hydrogen atoms.

Particularly stable structures result if hydrogen pairs are organized in such a way that the individual hydrogen atoms become part of more than one pair. This situation is realized in various model structures with hydrogen chains and networks.

Generally, the lowering of the total energy due to hydrogen ordering is more effective for hydrogen atoms at tetrahedral interstitial sites than for hydrogen atoms at octahedral sites; i.e., hydrogen ordering counteracts the site preference observed for unpaired hydrogen atoms. Comparing, e.g., the energetical sequence of unit cells with 64 lanthanum atoms in dhcp arrangement and translationally periodic chains of four hydrogen atoms, chains of tetrahedrally coordinated hydrogen atoms with a preferential direction parallel to the *c* axis have turned out to be the most stable such that the site preference is reversed in the case of these chain structures.

The propounded ordering mechanism indicates similarities between the solid solution of hydrogen in lanthanum and the solid solutions of hydrogen in the hcp metals scandium and yttrium as well as some heavier rare-earth metals with hcp structure, for which the formation of analogous pairs and the chainlike orientation of pairs are observed experimentally. The connectivity of the hydrogen chains in the mentioned metals with hcp structure, which cannot accommodate hydrogen atoms being part of more than one hydrogen pair, is different from the favorable chains of tetrahedrally coordinated hydrogen atoms in lanthanum. The insinuated similarity only refers to the basic structural elements, i.e., the hydrogen pairs.

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