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# H–H interactions in the superstoichiometric rare-earth dihydrides $RH_{2+c}$

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**Abstract**

Chemically similar compounds $LaH_{2+c}$ and $CeH_{2+c}$ reveal qualitatively different scenario of the ordering process, that can be associated with different values of the energy parameter $p$. There is made an attempt to understand the reasons of the different behavior of the ordering subsystems.
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## 1. Introduction

### 1.1. The system under consideration

In the superstoichiometric rare-earth dihydrides $RH_{2+c}$ (R = rare-earth atoms, H = hydrogen atoms) $N$ metal atoms form a f.c.c. lattice, while $(2+c)$N hydrogens are located in the interstitial sites of this lattice: $2N$ H-atoms fill $2N$ tetrahedral interstitial sites (they are called $H_T$-atoms) and $cN$ ($c \leq 1$) H-atoms are distributed among $N$ octahedral interstitial sites (they are called $H_O$-atoms) [1]. $N$ octa-interstitial sites form a simple f.c.c. lattice. The $cN$ $H_O$-atoms and their $(1-c)N$ vacancies distributed on the octa-interstitial sites can be treated as a binary substitutional ordering alloy with concentration $c$.

In corresponding conditions the $H_O$-atoms form some ordered configurations associated with two superstructure wave vectors [2],

$$\mathbf{k}_1 = (2\pi/a)\,(1\,0\,0), \quad \mathbf{k}_2 = (2\pi/a)\,(1/2\,0\,1), \tag{1}$$

and described by the distribution function $n(x, y, z)$ containing two long-range-order parameters, $\eta_1$ and $\eta_2$ [3]. The latter is presented by the expression [2–5]:

$$n(x, y, z) = c + \eta_1\gamma \exp(i2\pi x) + 2\eta_2\gamma \cos \pi(x + 2z), \tag{2}$$

Here $n(x, y, z)$ characterize the probability that the lattice site with coordinates $(x, y, z)$ is occupied by a $H_O$-atom, $c$ is the concentration of binary alloy, and $\gamma = 0.25$ is a normalizing factor. Function (2) takes three different values on the set of the given f.c.c. lattice sites:

$$n_1 = c + \eta_1\gamma + 2\eta_2\gamma, \quad n_2 = c + \eta_1\gamma - 2\eta_2\gamma,$$
$$n_3 = c - \eta_1\gamma. \tag{3a}$$

Occupation numbers $n_1$, $n_2$ and $n_3$ are restricted by conditions,

$$0 \leq n_i \leq 1, \quad (i = 1, 2, 3). \tag{3b}$$

Respectively, in the $(\eta_1, \eta_2)$-plane there is determined a region (see polygon [0 *c b d a* 0] in Fig. 1) which contains all positive values of LRO-parameters satisfying conditions (3a)–(3b).

It is known that hydrogen ordering is due to the H–H interaction. In the compounds under consideration this interaction is conditioned mainly by deformations of the host lattice induced by interstitial H-atoms. The corresponding interaction energy of the ordering subsystem usually is written as [3]:

$$E(\eta_1, \eta_2) = (1/2)\,\Sigma_{\mathbf{r}i,\,\mathbf{r}j}\, V(\mathbf{r}_i - \mathbf{r}_j)n(\mathbf{r}_i)n(\mathbf{r}_j), \tag{4}$$

where $V(\mathbf{r}_i - \mathbf{r}_j)$ is the H–H interaction potential between the H-atoms located in the lattice sites $\mathbf{r}_i$ and $\mathbf{r}_j$, while $n(\mathbf{r}_i)$ and $n(\mathbf{r}_j)$ are the probabilities that the sites $\mathbf{r}_i$ and $\mathbf{r}_j$ are really occupied by $H_O$-atoms. In the case of the distribution function (2) expression (4) gives:

$$E(\eta_1, \eta_2) = (Nk_B/2)[V_0c^2 + V_1(\gamma\eta_1)^2 + 2V_2(\gamma\eta_2)^2], \tag{5a}$$

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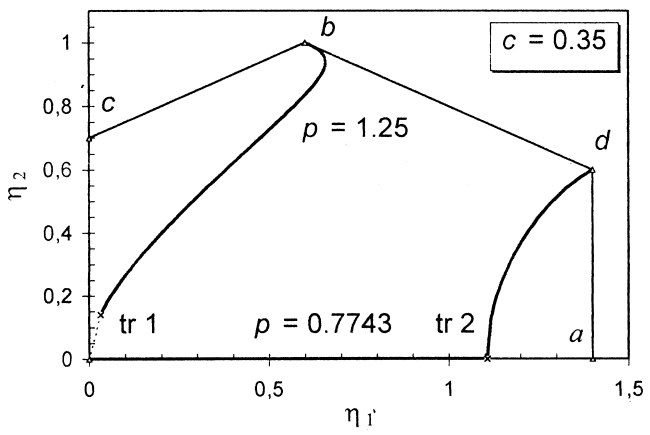


Fig. 1. Trajectories of ordering processes in $LaH_{2.35}$ ($p=0.7743$) and $CeH_{2.35}$ ($p=1.25$). [Sequences of equilibrium ordered states at gradually lowered temperatures characterized by the values of order parameters ($\eta_1(T)$, $\eta_2(T)$).] (0, 0)-point corresponds to the high-temperature disordered state, coordinates of the corner points $b$ and $d$, [$\eta_1(b)$, $\eta_2(b)$] and [$\eta_1(d)$, $\eta_2(d)$], represent the ordered states equilibrium at $T=0$ K in $CeH_{2.35}$ and $LaH_{2.35}$, respectively.

where $k_B$ is the Boltzmann constant and

$$V_0 \equiv V(\mathbf{k}_0)/k_B, \quad V_1 \equiv V(\mathbf{k}_1)/k_B, \quad V_2 \equiv V(\mathbf{k}_2)/k_B, \tag{5b}$$

are the Fourier-components of the potential $V(\mathbf{r}_i - \mathrm{r}_j)$, taken in the temperature units and corresponding to the superstructure wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ mentioned above, and $\mathbf{k}_0=0$.

The ordering implies that $V_1<0$ and $V_2<0$, while the sign of $V_0$ is unrestricted.

### 1.2. The problem under consideration

Let us introduce the energy parameter $p$ of the ordering subsystem, defined as the ratio of energy Fourier-components $V_2$ and $V_1$:

$$p \equiv V_2/V_1 \quad (p>0). \tag{6}$$

It was shown previously [4,5] that the sequence of equilibrium ordered states (the trajectory of the ordering process in the ($\eta_1$, $\eta_2$)-plane) is qualitatively different in the systems with different values of concentration $c$ and energy parameter $p$.

It is interesting to note that such structurally similar systems as $LaH_{2+c}$ and $CeH_{2+c}$ are characterized by qualitatively different values of $p$:$p(LaH_{2+c})=0.7743<1$, while $p(CeH_{2+c})\cong 1.25>1$. As a result, the ordering processes in these compounds even for the same value of concentration ($c=0.35$) are developed according to different scenarios and include qualitatively different sequences of equilibrium states (see Fig. 1). Particularly, for $CeH_{2.35}$ we have a one-step process ($0-b$) with a discontinuous disorder–order transition (0, 0)$\rightarrow$($\eta_1$, $\eta_2$). In $LaH_{2.35}$ there is a two-step process ($0-d$) containing disorder–order (0, 0)$\rightarrow$($\eta_1$, 0) and order–order ($\eta_1$, 0)$\rightarrow$($\eta_1$, $\eta_2$) continuous transitions.

The aim of the present publication can be formulated as an attempt to determine the main reasons of the differences of $p$-parameter values in the case of structurally similar systems, such as $LaH_{2+c}$ and $CeH_{2+c}$.

## 2. Analytical consideration

### 2.1. Mathematical conditions

Let us consider the interaction potential Fourier-components $V(\mathbf{k}_i)$, defined as

$$V(\mathbf{k}_i) = \Sigma_{\mathbf{r}j}\, V(\mathbf{r}_0 - \mathbf{r}_j)\exp[i\mathbf{k}_i(\mathbf{r}_0 - \mathbf{r}_j)]. \tag{7}$$

In the case of f.c.c. lattice the latter expression for the wave vectors (1) gives:

$$V(\mathbf{k}_0) = 12\omega_1 + 6\omega_2 + 24\omega_3 + 12\omega_4 + 24\omega_5 + 8\omega_6 + 48\omega_7 + 6\omega_8 \ldots \tag{8a}$$

$$V(\mathbf{k}_1) = -4\omega_1 + 6\omega_2 - 8\omega_3 + 12\omega_4 - 8\omega_5 + 8\omega_6 - 16\omega_7 + 6\omega_8 \ldots \tag{8b}$$

$$V(\mathbf{k}_2) = -4\omega_1 + 2\omega_2 + 8\omega_3 - 4\omega_4 - 8\omega_5 - 8\omega_6 + 16\omega_7 + 6\omega_8 \ldots \tag{8c}$$

where $\omega_1$, $\omega_2$, $\omega_3$, etc. denote the H–H interaction potential values $V(\mathbf{r}_0 - \mathbf{r}_j)$ for those pairs of hydrogen atoms which are separated by the distances equal to the radius of the first, second, third, etc., coordination spheres, respectively. In the units of the f.c.c. lattice constant $a$ the radii of these spheres are as follows:

$$r_1 = (1/2)^{1/2}, r_2 = 1, r_3 = (3/2)^{1/2}, r_4 = (2)^{1/2},$$
$$r_5 = (5/2)^{1/2}, r_6 = (3)^{1/2}, r_7 = (7/2)^{1/2}, r_8 = 2. \tag{9}$$

Taking into account that $V(\mathbf{k}_1)<0$ and $V(\mathbf{k}_2)<0$, let us consider the difference

$$\Delta V(\mathbf{k}_2, \mathbf{k}_1) \equiv -[V(\mathbf{k}_2) - V(\mathbf{k}_1)]. \tag{10}$$

The sign of $\Delta V(\mathbf{k}_2, \mathbf{k}_1)$ reflects the value of energy parameter $p$. Particularly, from (10) it follows that when $\Delta V(\mathbf{k}_2, \mathbf{k}_1)>0$, then $|V(\mathbf{k}_2)|>|V(\mathbf{k}_1)|$ indicating that $p>1$, while when $p<1$, then, respectively, $|V(\mathbf{k}_2)|<|V(\mathbf{k}_1)|$ and $\Delta V(\mathbf{k}_2, \mathbf{k}_1)<0$.

From (8b) and (8c) it follows:

$$\Delta V(\mathbf{k}_2, \mathbf{k}_1) = 4\,[\omega_2 + 4(\omega_4 + \omega_6)] - 16(\omega_3 + 2\omega_7). \tag{11}$$

It means that the sign of $\Delta V(\mathbf{k}_2, \mathbf{k}_1)$ (and the value of $p$) is determined by the difference $\{[(1/4)\omega_2 + \omega_4 + \omega_6] - [\omega_3 + 2\omega_7]\}$. If additionally we assume that all $\omega_i$ are

positive, then it can be deduced that the condition $\Delta V(\mathbf{k}_2, \mathbf{k}_1) > 0$ is associated with the inequality

$$[(1/4)\omega_2 + (\omega_4 + \omega_6)] > (\omega_3 + 2\omega_7). \quad (12)$$

Thus, it can be formulated a statement: in $CeH_{2+c}$-like compounds the distance dependence of the H–H interaction potential $V(r)$ satisfies the inequality (12) that provides $p(CeH_{2+c}) > 1$, while in $LaH_{2+c}$-like compounds this condition is not fulfilled and, as a result, $p(LaH_{2+c}) < 1$.

### 2.2. Physical background of the mathematical condition

Condition (11) is sufficiently general. Particularly, we have not specified the signs of the potential energy values $\omega_i$. If we assume a monotone, simplest distance dependence of the H–H interaction $V(r)$,

$$V(r) = V^0/r^\alpha, \quad (13)$$

then we can write

$$\omega_i = V^0/r_i^\alpha. \quad (14)$$

Taking into account the radii of the coordination spheres (9), we obtain:

$$\begin{aligned} &\omega_1 = A(2)^{\alpha/2}, \omega_2 = A(1)^{\alpha/2}, \omega_3 = A(2/3)^{\alpha/2}, \\ &\omega_4 = A(1/2)^{\alpha/2}, \omega_5 = A(2/5)^{\alpha/2}, \omega_6 = A(1/3)^{\alpha/2}, \\ &\omega_7 = A(2/7)^{\alpha/2}, \omega_8 = A(1/4)^{\alpha/2}, \end{aligned} \quad (15)$$

where $A \equiv V^0/a^\alpha$. Introducing these expressions in (8b) and (8c) we can estimate that in the case of $\alpha > 1$ conditions $V(\mathbf{k}_1) < 0$ and $V(\mathbf{k}_2) < 0$ lead to the requirement $V^0 > 0$, i.e., $A > 0$. It follows, particularly, that all potential energy values $\omega_i$ are positive, in accordance with the above assumption, and that, consequently, condition (12) turns to be valuable for the analyses of the considered compounds.

Within the frames of above definitions, expression (11) can be written as

$$\Delta V(\mathbf{k}_2, \mathbf{k}_1) = -16A[f(\alpha') - (1/4)]. \quad (16)$$

where $\alpha' \equiv \alpha/2$ and

$$f(\alpha') \equiv (2/3)^{\alpha'} + 2(2/7)^{\alpha'} - (1/2)^{\alpha'} - (1/3)^{\alpha'}. \quad (17)$$

Then the condition

$$f(\alpha') > 1/4. \quad (18)$$

leads to $\Delta V(\mathbf{k}_2, \mathbf{k}_1) < 0$ providing $p < 1$.

Direct numerical estimations of function (17) indicate that condition (18) is satisfied within the interval of $\alpha'$ values: $0 \le \alpha' \le 2$, i.e., for $0 \le \alpha \le 4$. Consequently, we conclude that in the systems where at distances $0 < r \le 2a$ potential $V(r)$ falls more rapidly than $1/r^4$ (i.e., $\alpha > 4$), condition (18) is not fulfilled and we obtain $\Delta V(\mathbf{k}_2, \mathbf{k}_1) > 0$ providing $p > 1$, while in the systems where $p < 1$ we have to suppose that the distance dependence of the interaction potential behaves as $1/r^4$, or it is slower.

The above consideration allows us to analyze structurally identical compounds $LaH_{2+c}$ and $CeH_{2+c}$. Particularly, it can be supposed that the difference between these systems can be ascribed to the different shapes of H–H interactions: in the case of compounds $CeH_{2+c}$ the $V(r)$ potential at distances $0 < r \le 2a$ falls more rapidly than $1/r^4$ providing $p(CeH_{2+c}) > 1$, while in $LaH_{2+c}$ the function $V(r)$ seems to vary, in contrast, more gradually and the relation $p(LaH_{2+c}) < 1$ is realized.

The difference between $V(r)[LaH_{2+c}]$ and $V(r)[CeH_{2+c}]$ functions presumably may be associated with the different elastic properties of the metal sublattices in the corresponding dihydrides $RH_2$.

## 3. Discussion

It must be stressed that we need information concerning the properties of the *metal f.c.c. sublattice* in the $RH_2$ compounds with $CaF_2$-structure (which differ significantly from the properties of the *host h.c.p. lattices* of corresponding R-metals).

Unfortunately, experimental information on the elastic properties of $RH_2$ compounds is poor (see, e.g., Ref. [1]) and we are able to perform some indirect estimations only.

Information on elastic moduli of crystal lattices is contained in a number of physical parameters. It is known [6] that the characteristic Debye temperature $\theta_D$ is related to the Young's modulus of the lattice $E$. An approximate relationship between these two parameters in the case of a f.c.c. lattice can be presented as [7]:

$$\theta_D \approx 12[Ea/A]^{1/2}, \quad (19)$$

where $A$ is the atomic weight (in atomic units), $a$ is the lattice constant (in Å), and $E$ is given in $kg/mm^2$. (Numerical values of $\theta_D$ are in K.)

The upper limit of the lattice vibrational spectrum is determined in the heat capacity and X-ray measurements as Debye temperature $\theta_D$ and in electrical resistance measurements as the Grüneizen temperature $\theta_G$ [6]. Numerical values of $\theta_D$ and $\theta_G$ are usually sufficiently close [6,7]. The available experimental values of temperatures $\theta_D$ and $\theta_G$, determined in rare-earth dihydrides are collected in (Ref. [1], Table 16).

At the same time it was announced [8] that the Debye temperatures of metal hydrides $MH_x\theta_D$ ($MH_x$) can be estimated, in principle, basing upon the known values $\theta_D$ (M) of the corresponding host metal lattices. It was established an empirical relationship for the metal hydrides [8]:

$$[\theta_D(MH_x)]^2 = 0.038[\theta_D(M)]^2|\Delta H_f(x)|^{0.87}, \quad (20)$$

where $\Delta H_f(x)$ is the heat of formation of the $MH_x$ hydride (taken in the units [kJ/mol $H_2$]).

But this simple expression seems to be inapplicable in the case of the rare-earth dihydrides $RH_2$. As an example, let us consider the case of compounds $LaH_2$ and $TbH_2$.

From (20) it follows that $\theta_D(TbH_2) > \theta_D(LaH_2)$ [as $\theta_D(Tb) = 155 > \theta_D(La) = 135$ K (Table 15 in Ref. [9]) and $\Delta H_f(TbH_2) > \Delta H_f(LaH_2)$ (Table 15 in Ref. [1]), while experimental results indicate that $\theta_G(TbH_2) < \theta_D(LaH_2)$ (see Table 16 in Ref. [1]). The contradiction is obvious.

Continuing the discussion of the dihydrides $LaH_2$ and $TbH_2$ we shall try to compare their elastic properties.

Basing upon the above-mentioned experimental characteristic temperatures of these compounds (see Table 16 in Ref. [1]) we have to take $\theta_D(LaH_2) \cong 340$ K (in accordance with Ref. [10]) and $\theta_G(TbH_2) \cong 240$ K. Then using (19) it can be deduced:

$$E(LaH_2) \approx 17.7\ 10^3\ \mathrm{kg/mm^2},$$

$$E(TbH_2) \approx 12.3\ 10^3\ \mathrm{kg/mm^2}. \quad (21)$$

(It was supposed that a $(LaH_2) = 5.6698$ Å, a $(TbH_2) = 5.2495$ Å (Table 5 in Ref. [1]), and that in the case of acoustic branch of lattice vibrations $A(LaH_2) \cong (139 + 2)$ and $A(TbH_2) \cong (159 + 2)$).

We must not overestimate the significance of the numerical values (21), but some qualitative conclusions may be derived.

As $E(TbH_2) < E(LaH_2)$, it seems that the displacement fields in the $TbH_2$-lattice caused by the interstitial H-atoms should be *more short-ranged* than those in the $LaH_2$-lattice. Thus, it can be expected that $\alpha(TbH_{2+c}) > \alpha(LaH_{2+c})$ providing the realization of the inequality: $p(TbH_{2+c}) > p(LaH_{2+c})$. This result is in accordance with the energy parameter $p$ values estimated in our previous investigations-$p(TbH_{2+c}) \cong 1$ [11] and $p(LaH_{2+c}) \cong 0.7743$ [5].

The absence of information on the elastic properties of dihydride $CeH_{2+c}$ makes impossible to repeat the above consideration on the pair of compounds $LaH_{2+c}$ and $CeH_{2+c}$. We intend to discuss this problem in the future.

## 4. Summary

We have analyzed the specific character of H–H interaction in the superstoichiometric dihydrides of different lanthanides and have formulated mathematical conditions (12), (18) which relate the value of the energy parameter $p$ with the distance dependence of the H–H interaction potential $V(r)$.

These conditions are very approximative, as (a) expression (11) was formulated taking into account a restricted number of coordination spheres, and (b) condition (18) follows from the assumption of a simplest dependence (14).

A lack of experimental information concerning the elastic properties of $RH_2$ compounds makes it difficult to check the results of our treatment quantitatively.

We hope that in spite of the mentioned above restrictions the described scheme of consideration of the energy parameter $p$ will be useful in practice.

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