

Physics

“Anomalous” Heat Capacity of the Stoichiometric Lanthanum Dihydride

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ABSTRACT. Two models aimed to describe the experimentally registered difference between the heat capacity temperature dependences $C(T)$ of dihydrides LaH_2 and CeH_2 , denoted as $C(T)[\text{LaH}_2]$ and $C(T)[\text{CeH}_2]$ are compared. In both models the specific features of the $C(T)[\text{LaH}_2]$ are ascribed to the transfer of a number of hydrogen atoms from energetically favorable tetrahedral interstitial positions to the less-favorable octahedral interstitial positions. One of the models allows random transitions from tetra-positions into octa-positions of a number of separate H-particles, while the second model implies that in the *fcc* crystalline lattice of metal atoms linear hydrogen-metal atomic complexes - “H-M-H dumbbells” are formed. In the ground state they are oriented along [111]-type crystallographic directions and at temperature increasing they are reoriented along the [100]-type crystallographic directions. Existing experimental results give preference to the first model. It is suggested that analogous tetra-octa transfers are not realized in cerium dihydride due to the specific details of the H-H interactions in the cerium lattice. © 2013 Bull. Georg. Natl. Acad. Sci.

Key words: rare-earth hydrides, redistribution of interstitial atoms, total heat capacity of hydrides.

Stoichiometric and superstoichiometric dihydrides of lanthanum and cerium - LaH_x and CeH_x ($x = 2 + c$; $c = 0$ for stoichiometric and $0 < c \leq 1$ for superstoichiometric dihydrides) are very well known compounds today [1]. They have *fcc* crystalline lattices of N metal atoms (M-atoms) containing $(2 + c)N$ hydrogen atoms (H-atoms) which are located in tetrahedral and octahedral interstitial positions: $2NH$ -atoms are assumed to fill the set of $2N$ tetra-positions (“ H_t atoms”), while “additional” cN H-atoms are distributed on the set of N octa-positions (“ H_o atoms”). When the number of H_o -atoms is less than

the number of octa-positions ($c < 1$), then at low temperatures they form ordered spatial configurations described by some distribution function containing two long-range-order (LRO) parameters. It is significant to note that ordered configurations in both hydrides, LaH_{2+c} and CeH_{2+c} , are characterized by an identical distribution function [2]. In spite of this likeness, there exists a remarkable difference in the behavior of the ordering subsystems of these two compounds. This difference is caused by different values of the characteristic energy constants of the ordering subsystems, denoted as V_1 and V_2 (see [2])

and particularly, by the difference of the energy constants ratios $p \equiv V_2 / V_1$. It was established (see e.g. [2]) that $p[\text{LaH}_x] = 0.7743 < 1$ and $p[\text{CeH}_x] = 1.25 > 1$.

The heat capacity of a binary metallic nonmagnetic alloy $C(T)$ is usually presented as the sum of the following terms

$$C(T) = C_{ac} + C_{op} + C_{el}, \quad (1)$$

where C_{ac} is the part of the total heat capacity associated with acoustic waves in the subsystem of metal atoms, C_{op} is caused by local vibrations of light interstitial particles and C_{el} is the part induced by conduction electrons. When light particles are located in different interstitial positions (e.g. in tetrahedral and octahedral positions) then they will be characterized by different local frequencies ν_t and ν_o , and will provide different inputs to the total heat capacity ($C_{op}(t)$ and $C_{op}(o)$, respectively).

The ordering process developed in the subsystem of H_o -atoms provides an additional specific term which will be discussed below.

Thus, in the case of ordering rare-earth metallic dihydrides the heat capacity of compounds can be generally presented as

$$C(T) = C_{ac} + C_{op}(t) + C_{op}(o) + C_{el} + C_{ord}. \quad (1')$$

Scheme of calculations. Formulae for calculation of the main heat capacity ingredients C_{ac} , C_{op} and C_{el} are well known [3]. They were reproduced already in [4] and we shall not repeat them here. The term associated with acoustic waves is characterized by the maximal allowed frequency of acoustic waves ν_{max} , or by the corresponding "Debye temperature T_D " determined as $T_D = h\nu_{max} / k_B$ (k_B – the Boltzmann constant). Terms related to high-frequency local oscillations of light particles are characterized by the frequency values $\nu_{loc}(t)$ (for tetra-interstitial positions) and $\nu_{loc}(o)$ (for octa-interstitial positions), or by the corresponding "Einstein temperatures", determined as $T_E(t) = h\nu_{loc}(t)/k_B$ and $T_E(o) = h\nu_{loc}(o)/k_B$, respectively.

Thus, to describe the "lattice part" of the total heat capacity - $C_L(T) = C_{ac}(T) + C_{op}(T)$, $C_{op}(T) = C_{ac}(t)(T) + C_{op}(o)(T)$ - we have to define for each

given dihydride the set of energy parameters - T_D , $T_E(t)$ and $T_E(o)$.

The heat capacity part induced in metallic compounds by conduction electrons, written usually as $C_{el} = gT$ [3], contains the constant g (defined in [cal / mole K²] units) which is proportional to the density of electronic states at the Fermi level (or, finally, to the number of "free electrons per metallic ion").

The heat capacity of the subsystem of ordering particles is determined in the following way. We calculate the set of equilibrium energies of the ordering subsystem $E_{ord}(T)$ in a wide range of temperatures and then define $C_{ord}(T)$ as

$$C_{ord}(T) = dE_{ord}(T) / dT.$$

It was enounced [5] that in the lanthanum dihydride there can be formed linear complexes - $M-H$ dumbbells. If we take into account this model then hydrogen redistribution between tetra- and octa-positions can be presented as spatial reorientation of existing "dumbbells". Particularly, in *fcc* lattices hydrogen in tetra-position corresponds to dumbbell oriented along [111]-type crystallographic directions, while H-atoms in octa-positions correspond to the dumbbells oriented along [100]-type directions. If we ascribe to each direction different energy levels (E_t for the [111]-type orientation, and E_o for the [100]-type orientation), then our system of dumbbells can be considered as a well-known "two-level system" characterized by the difference between energy levels $D = |E_t - E_o|$. It is known that such system reveals a "Schottky-type" heat capacity [3]. Within the frames of the "dumbbells-reorientation model" instead of expression (12) we have to write

$$C(T) = C_{ac} + C_{op}(t) + C_{op}(o) + C_{el} + C_{re}, \quad (1'')$$

where C_{re} denotes the dumbbell reorientation induced heat capacity part (see below).

Thus, successful application of the above mentioned standard mathematical expressions representing different parts of the total heat capacity imply knowledge of the following energy parameters: T_D , $T_E(t)$, $T_E(o)$, g , V_1 , V_2 , E_t and E_o .

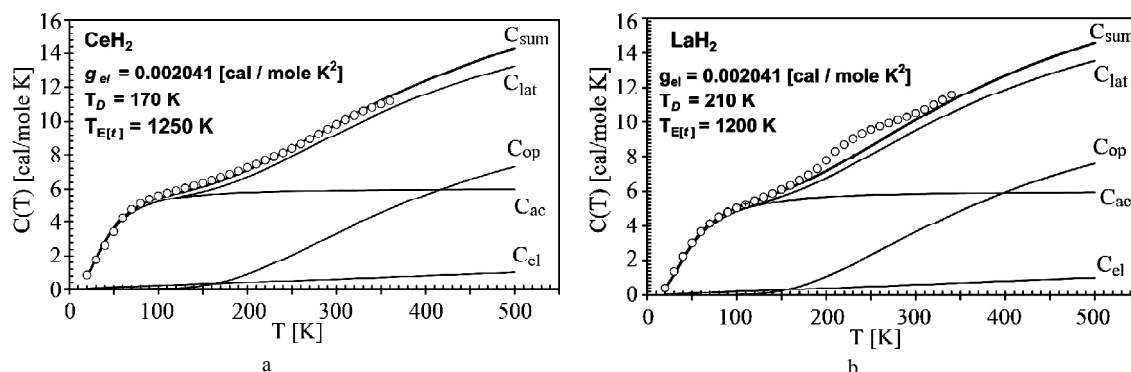


Fig. 1. Description of experimental heat capacity temperature dependences $C(T)$ for CeH_2 (Fig. 1a) and LaH_2 (Fig. 1b). Sequences of circles – experimental data, solid lines – results of calculations. (For details see text).

Experimental information. Heat capacities $C(T)$ of dihydrides LaH_2 and CeH_2 were measured within the temperature range 5 – 360 K [6,7]. These $C(T)$ dependences are shown in Figs. 1a and 1b by the sequences of circles. Corresponding $C(T)$ calculations were based on expression (1). Thin solid lines in Fig. 1 represent temperature dependences of C_{ac} , C_{op} and C_{el} ; C_{lat} denotes $(C_{ac} + C_{op})$. The summary heat capacities of metal dihydrides $C_{sum} = C_{lat} + C_{el}$ are given by thick solid lines. This numerical analyses of experimental data clearly reflect the “anomalous” behavior of lanthanum dihydride. It was already pointed out [4] that the heat capacity of stoichiometric cerium dihydride seems to be an example of “classical” unperturbed collection of all H-atoms in interstitial tetra-positions, while in the case of stoichiometric LaH_2 such assumption provides significant discrepancy between the experimental and analytical $C(T)$ dependences (see Fig.1b). It was mentioned as well [4] that in the dihydride LaH_2 a number of H-atoms seems to be transferred into octa-positions and oscillate with some different local frequency. Below we consider two models aimed to describe these “tetra-octa” hydrogen displacements.

Mathematical details. We assume that N_H total number of H-atoms are distributed among $N_t = 2N$ tetra-positions and $N_o = N$ octa-positions. The numbers of H-atoms in t -sites and o -sites are denoted as $N_H(t)$ and $N_H(o)$. Evidently, $N_H(t) + N_H(o) = N_H$.

Concentrations of H-atoms in the given compound as a whole and in the interstitial positions of

both types are denoted respectively as x , $c(t)$ and $c(o)$. They are determined as

$$x = N_H / N, \quad c(t) = N_H(t) / N, \quad c(o) = N_H(o) / N.$$

It follows that

$$c(t) + c(o) = x. \quad (2)$$

We investigate the case when $x = 2 = const.$, but $c(t)$ and $c(o)$ are considered to be variables restricted by condition (2).

In our previous investigations we considered ordering processes developed in the subsystem of H-atoms located in octa-positions (H_o -atoms) on assuming $c(o) = const$. Now this parameter becomes variable and only the total concentration of H-atoms x remains constant. As a result, the free-energy function of the subsystem of H-atoms $F(c(t), c(o); T)$ except the traditional part related to the ordering processes in octa-positions $F_{ord}(c(o); T)$ will contain an additional part associated with hydrogen redistribution between t -sites and o -sites. We call the latter term *configuration free energy* and denote it $F_{conf}(c(t), c(o); T)$. Thus, the total free-energy function of the hydrogen subsystem $F(c(t), c(o); T)$ can be represented as

$$F(c(t), c(o); T) = F_{conf}(c(t), c(o); T) + F_{ord}(c(o); T) \quad (3)$$

Equilibrium states of the given $M-H$ compound are associated with the minimal values of function (3).

The next steps of the free-energy minima calculations depend on the model which we use to describe

the hydrogen subsystem. Below we shall analyze two tentative models. The first one is the “*hydrogen redistribution model*”. It implies consideration of hydrogen subsystem as a totality of particles distributed between the sites characterized by different potential wells. The second model called “*hydrogen dumbbells reorientation model*” assumes that in dihydride LaH_2 exist linear H-M-H dumbbells oriented in different spatial directions. As it was mentioned above, population of *o*-sites by H-atoms is considered here as a result of spatial reorientation of linear MH_2 dumbbells from [111]-type “tetra-directions” towards [100]-type “octa-directions”.

Hydrogen redistribution model. The free-energy function of the system is given by expression (3), where

$$F_{conf}(c(t), c(o); T) = E_{conf}(c(t), c(o)) - TS_{conf}(c(t), c(o)) \quad (4a)$$

and

$$F_{ord}(c(o); T) = E(c(o); T) - TS(c(o); T). \quad (4b)$$

The minimal value of function (4a) determines the equilibrium distribution of H-atoms between the *t*-sites and *o*-sites at the given temperature T (i.e. determines equilibrium values of $N_H(t)$ and $N_H(o)$). Ordered distribution of $N_H(o)$ hydrogen atoms on the set of *o*-sites is determined by function (4b).

Let us consider first expression (4a) taking into account two well-established features of both systems. It is known [1] that both hydrides, LaH_x and CeH_x , are stable within the whole range $2 \leq x \leq 3$, and in both systems preferentially are occupied *t*-sites. It follows that if we ascribe to interstitial tetra- and octa-positions some potential wells - V_t and V_o , respectively - then we have to assume that $V_t, V_o < 0$ and $|V_t| > |V_o|$.

In these conditions the internal energy term in $F_{conf}(c(t), c(o))$ can be written as:

$$E_{conf}(c(t), c(o)) = N_H(t) V_t + N_H(o) V_o = (N_H - N_H(o)) V_t + N_H(o) V_o$$

or

$$E_{conf}(x, c(o)) = N[xV_t + c(o)(V_o - V_t)] \quad (5)$$

The corresponding entropy function for the hydrogen tetra-octa redistribution process can be generally presented as $S_{conf}(c(t), c(o)) = k_B \ln W$, where $W = (N_t + N_o)! / [N_H(t)! (N_H - N_H(t))! N_H(o)! (N_o - N_H(o))!]$.

After traditional algebraic procedures the last expression reduces to the following relation

$$S_{conf}(c(t), c(o)) = -Nk_B \{ [c(o) \ln(c(o)) + (1 - c(o)) \ln(1 - c(o))] + [c(t) \ln(c(t)) + (2 - c(t)) \ln(2 - c(t))] \}. \quad (6)$$

Expressions (5) - (6) allow us to calculate numerical values of $F_{conf}(c(t), c(o), T)$.

Spatially ordered configuration of H_o -atoms is described by the distribution function $n(xyz)$ containing two long-range-order (LRO) parameters - η_1 and η_2 . It looks like [2]

$$n(x, y, z) = c(o) + \eta_1 \gamma \exp[i 2px] + 2\eta_2 \gamma \cos[p(x + 2y)], \quad (7a)$$

where $\gamma = 0.25$ is a normalizing factor.

On the set of *fcc* lattice sites function (7a) obtains three different values - n_1, n_2 and n_3 :

$$\begin{aligned} n_1 &= c(o) + \eta_1 \gamma + 2\eta_2 \gamma, \\ n_2 &= c(o) + \eta_1 \gamma - 2\eta_2 \gamma, \\ n_3 &= c(o) - \eta_1 \gamma. \end{aligned} \quad (7b)$$

Conditions $0 \leq n_1, n_2, n_3 \leq 1$ and relations (7b) restrict the region of allowed values of order parameters η_1 and η_2 (see the region *ocda0* in Fig. 2). The spatial ordering is described by the “trajectory of the process” in the (η_1, η_2) -plane - the sequence of points whose coordinates represent the pairs of equilibrium values of order parameters $\eta_1(T), \eta_2(T)$. (I.e. “the process trajectory” is a sequence of points, where are located the minima of the free-energy function (4b) at the gradually variable temperature T). A simplest example of such trajectory corresponding to concentration $c(o) = 0.14$ and energy parameter $p = 0.7743$ is given in Fig. 2. The disordered state is represented by the point $(\eta_1 = 0, \eta_2 = 0)$, while the low-tempera-

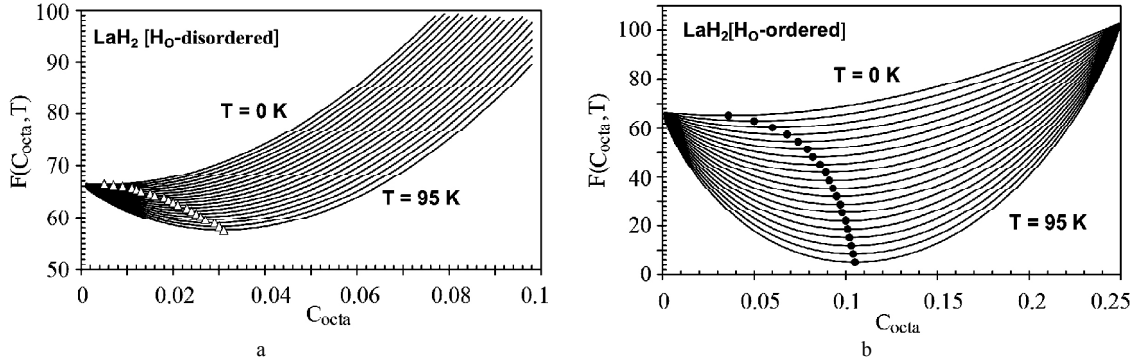


Fig. 2. Free-energy of the dihydride LaH_2 , considered as a function of hydrogen concentration in octa-positions at different temperatures T . [$0 \text{ K} \leq T \leq 95 \text{ K}$, $\Delta T = 5 \text{ K}$]
 a - disordered distribution of H_o -atoms; equilibrium states are denoted by triangles.
 b - maximally ordered configuration of H_o -atoms; equilibrium states are denoted by black points.

ture state of maximal order – by the corner point d with coordinates $[\eta_1 = c(o)/\gamma, \eta_2 = c(o)/\gamma]$. This ordered state is reached (at temperature lowering) along the solid line. (The dashed-line part of the trajectory indicates the discontinuous disorder-order transition).

Free energy function $F_{\text{ord}}(c(o); T)$ related to distribution function (7a) is as follows [2]:

$$F_{\text{ord}}(c(o); T) = Nk_B \{ 0.5 [V_0 c^2 + V_1 (\gamma \eta_1)^2 + 2V_2 (\gamma \eta_2)^2] + \sum_{i=1,2,3} m_i [n_i \ln n_i + (1-n_i) \ln(1-n_i)] \}, \quad (8)$$

where V_0, V_1 and V_2 are Fourier-components of the H_o - H_o interaction potential taken in temperature units (see e.g. [2]); $m_1 = m_2 = 0.25$ and $m_3 = 0.5$ are parts of octa-positions where function (7a) equals n_1, n_2 and n_3 , respectively.

Calculations of the system’s total free-energy function (3) were performed basing on expressions (5), (6) and (8), and the following relations between energy constants:

$$V_1(c(o)) = [-1880 + (c(o) - 0.25)1360] \text{ K},$$

$$V_2(c(o)) = 0.7743 V_1(c(o)) [2], \quad (9a)$$

$$V_o(c(o)) = -3 V_1(c(o)), \quad V_t = 0.01 V_o(c(o)),$$

$$V_o = 0.001 V_o(c(o)). \quad (9b)$$

Temperature was treated as a parameter and the role of independent variable is played by concentration of H_o -atoms $c(o)$ (indicated in both figures as c_{octa}).

Results of calculations within the temperature

range [0–95 K] with the steps $\Delta T = 5 \text{ K}$ are shown in Fig. 2a and Fig. 2b, representing respectively two limiting states of H_o -atoms – the disordered state (Fig. 2a) and the state of maximum order (Fig. 2b). Two basic conclusions follow.

a) At each considered temperature there exists a specific concentration of H_o -atoms $c(o)$ which corresponds to the minimum of the total free-energy function; at rising temperatures this minimum is displaced towards some limiting concentration value.

b) The free-energy minima are displaced towards larger values of concentration $c(o)$ when H_o - H_o interactions are added. In other words, H-H interactions stabilize the increased concentration of H-atoms in octa-positions.

In order to demonstrate the influence of hydrogen partial transfer from t -positions to o -positions on the total heat capacity of the lanthanum dihydride we present in Fig. 4 the results of our heat capacity calculations performed for the lanthanum dihydride within the frames of an assumption that $c(t) = 1.86$ and $c(o) = 0.14$. The characteristic energy parameters were selected as follows:

$$T_D = 210 \text{ K}, \quad T_{E(t)} = 1200 \text{ K}, \quad T_{E(o)} = 720 \text{ K},$$

$$g = 0.002041 [\text{cal/mole K}^2] \quad (10)$$

Hydrogen dumbbells reorientation model. It is assumed that dihydride LaH_2 consists of N linear dumbbells H-M-H, which are characterized by two different energy levels depending on their orientation with

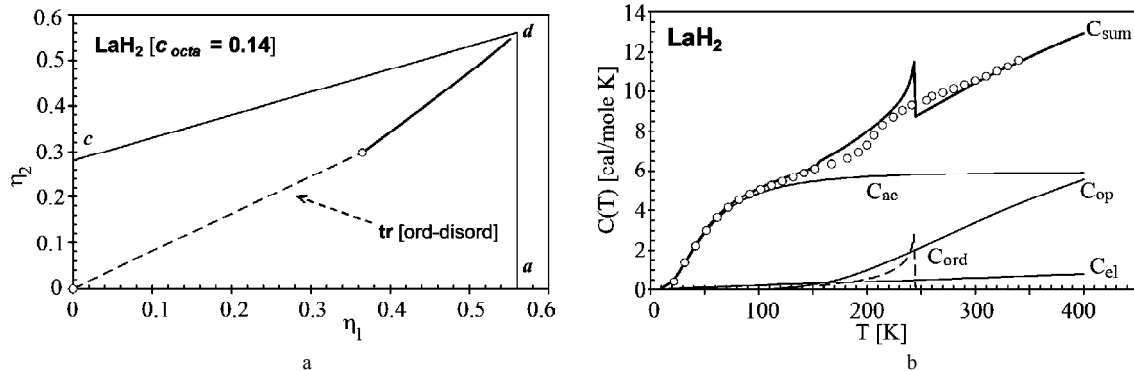


Fig. 3. Stoichiometric dihydride LaH_2 on assuming $c_{\text{octa}} \equiv c(o) = 0.14$ and $c_{\text{tetra}} \equiv c(t) = 1.86$. a - Trajectory of the ordering process of H_O -atoms. The high-temperature disordered state – point 0; the low-temperature state of maximal order – point d ; b - Experimental heat capacity results [6,7] (the sequence of circles) and their description by expression (1').

respect to crystallographic directions. The energy gap between these levels is assumed to be equal $\Delta \approx 500$ K. Corresponding additional heat capacity part associated with reorientation of dumbbells is the so-called “Schottky-term”, which in the case of two nondegenerate levels looks like [3]:

$$C_{re}(T) = R z^2 \exp[z] / (1 + \exp[z])^2, \\ z \equiv \Delta / T; \quad R = 2 \text{ [cal / mole K]} \quad (11)$$

We represent the total heat capacity of dihydride by relation (1'').

The next question is the number of H-M-H dumbbells in the lattice. In tetra-orientation [111] there can be formed N dumbbells, but in octa-orientations (along [100]-type axes) - not more than $N/2$ dumbbells (coming from the number of octa-sites). Thus the maximum number of “orientable” dumbbells must be not more than $N/2$. Basing on Fig. 3 it follows that equilibrium number of H-particles in octa-positions

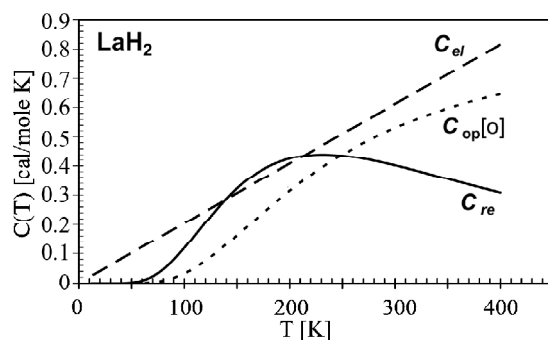


Fig. 4. The part of heat capacity $C_{re}(T)$ associated with reorientations of H-M-H dumbbells

is restricted, and no more than approximately 10 % of dumbbells can be reoriented. Calculations of the “reorientation heat capacity” (11) and of the total $C(T)$ dependence for the dihydride LaH_2 (based on expression (1'')) give results shown in Fig. 4 and Fig. 5, respectively. We see that though the additional reorientation process provides a maximum in the heat capacity temperature dependence (see Fig. 5a), it seems to be too wide and can not describe the experimentally registered anomaly of $C(T)$ dependence in lanthanum dihydride. Generally, it follows that application not only of the “H-M-H dumbbell model”, but of any “two-level” model giving an additional term (11) is ineffective for the considered system.

Concluding remarks. We have analyzed two tentative models aimed to explain the experimentally registered anomaly in the heat capacity of lanthanum dihydride. In spite of the published conclusions [5] concerning the possibility of existence of “hydrogen

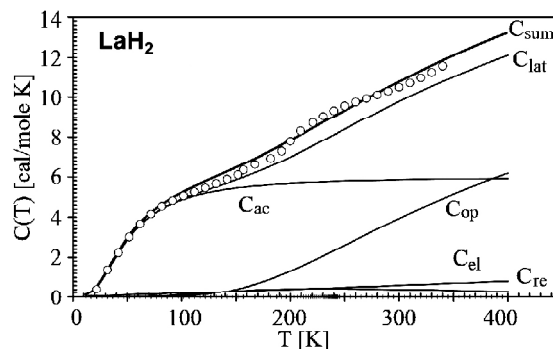


Fig. 5. Calculated total heat capacity including reorientations of H-M-H dumbbells. [$C_{lat} = C_{ae} + C_{op}$]

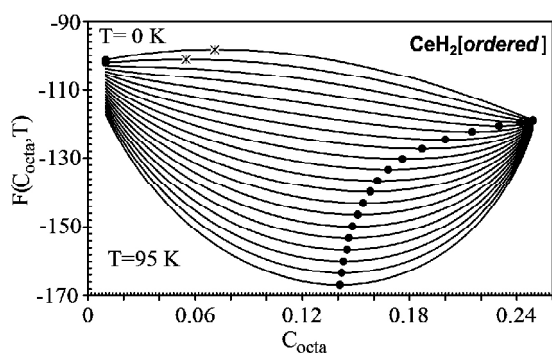


Fig. 6. The case of ordering cerium dihydride CeH_2 . Free-energy minima at different temperatures are denoted by black points. The free-energy maxima are denoted by crosses.

dumbbells” in lanthanum hydrides, the “dumbbells reorientation model” failed to reproduce the experimental $C(T)[LaH_2]$ dependence. It follows that the discussed heat capacity anomaly is related mainly to the temperature-dependent transfer of separate H-particles from energetically favorable tetra-positions to less favorable octa-positions. Ordering process in the subsystem of octa-hydrogens significantly stimulates this transfer. In order to reproduce adequately the experimentally established anomaly, in prospective analyses it seems necessary to take into account temperature dependence of the number of octa-hydrogen atoms.

There arises a natural question – why the given process of hydrogens redistribution does not take

place in the case of cerium dihydride. The answer is given in Fig. 6, where are presented the results of the free energy calculations performed for the ordering cerium dihydride (analogous to those shown in Fig. 2b). We see that in the case of the set of energy parameters established for CeH_{2+c} system [2], the minimal values of the system’s free energy function (denoted by black points in the picture) are associated with the relatively large octa-hydrogen concentration $c(o)$. At low temperatures they are separated from the “ $c(o) = 0$ state” by an energy maximum (denoted by crosses). Just due to these “energetic-details” (mainly due to condition $p[CeH_x] > 1$) possible tetra-octa fluctuation-induced transfers of light particles from tetra-positions to octa-positions are forbidden: sporadic transfers of separate particles are energetically unfavorable, and collective simultaneous transition of a sufficient number of particles cannot be realized by fluctuations. Respectively, the heat capacity of CeH_2 cannot be influenced by the redistribution processes analogous to those developed in lanthanum dihydride.

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ნაშრომში მოყვანილია ლანთანის დიჰიდრიდის სითბოტევადობის გამოთვლების შედეგები, რომლებიც ჩატარებულ იქნა ორი საგარეულო მოდელის ფარგლებში. ექსპერიმენტულ მონაცემებთან შედარების გზით გამოვლენილია უფრო პერსპექტიული მოდელი. ის გულისხმობს ტემპერატურის ზრდასთან ერთად წყალბადის ცალკეული ატომების გადასვლას “ენერგეტიკულად ხელსაყრელი” ტეტრაედრული კვანძის პოზიციებიდან ნაკლებად ხელსაყრელ ოქტაპოზიციებში. ხაზგასმულია, რომ LaH_{2+c} ნაერთებში ოქტაწყალბადების ქვესისტემაში არსებული ნაწილაკთა-შორისი ურთიერთქმედება ხელს უწყობს მათი გაზრდილი კონცენტრაციის სტაბილიზაციას. ლანთანის დიჰიდრიდის სითბოტევადობის აღნიშნული ანომალიის ზუსტი აღწერისათვის, როგორც ეტყობა, აუცილებელია გავითვალისწინოთ ოქტა-წყალბადების კონცენტრაციის ტემპერატურაზე დამოკიდებული ცვლადობა. მითითებულია ასევე, რომ ცერიუმის დიჰიდრიდის შემთხვევაში იგივე H-H ურთიერთქმედება დაბალი ტემპერატურების პირობებში ეწინააღმდეგება ნაწილაკების ფლუქტუაციურ გადასროლას ტეტრაპოზიციებიდან ოქტაპოზიციებში, ვინაიდან ოქტაწყალბადების წონასწორული მდგომარეობა ყალიბდება შედარებით მაღალ კონცენტრაციაზე, რომლის მიღწევასაც ხელს უშლის კონცენტრაციების საშუალო მნიშვნელობებისთვის არსებული პოტენციალური ბარიერი. სწორედ ამის გამო, ლანთანის დიჰიდრიდისაგან განსხვავებით, დაბალ ტემპერატურებამდე გაცვივებულ ცერიუმის დიჰიდრიდში ცალკეული H-ატომების გადასვლა ოქტაპოზიციებში იწვევს მისი თავისუფალი ენერჯის ზრდას, ნაწილაკთა მრავალრიცხოვანი ჯგუფის ერთდროული ფლუქტუაციური გადასვლა კი დაბალატემპერატურაზე.

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