

*Physics*

## Determination of Phase Transition Order Change Points in $\text{LaH}_{2+c}$ -Type Ordering Dihydrides

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**ABSTRACT.**  $\text{LaH}_{2+c}$ -type ordering hydrides are considered. Conditions which determine the values of critical concentrations associated with the phase transition type change and anomalously large heat capacity discontinuities are analyzed. © 2011 Bull. Georg. Natl. Acad. Sci.

**Key words:** rare-earth hydrides, ordering processes, phase transition anomalies.

The ordering superstoichiometric rare-earth dihydrides were widely investigated experimentally and theoretically (main experimental results were summarized in [1], for theoretical considerations see e.g. [2-9]). Numerical calculations [3-5] performed for the b-phases of  $\text{CeH}_{2+c}$  and  $\text{LaH}_{2+c}$  ( $0 < c < 0.8$ ) showed that in these compounds the ordering subsystem of hydrogen atoms located in octahedral interstitial sites ( $\text{H}_0$ -atoms) reveal a two-step ordering process containing the disorder-order and order-order transition points. As established [3, 5], in the cerium dihydrides  $\text{CeH}_{2+c}$  the disorder-order phase transition is continuous (similar to the second-order phase transitions) within the range  $[0.35 < c \leq 0.65]$ , and discontinuous (similar to the first-order phase transitions) outside of this region. In contrast, in the case of dihydride  $\text{LaH}_{2+c}$  within the concentration range  $[0 < c < 0.5]$  disorder-order transformation is continuous except the case of very low values of  $c$  ( $c < 0.1$ ), while order-order transition is discontinuous at concentrations  $c \leq 0.25$  and becomes continuous at higher concentrations [4, 5]. Precise numerical calculations [8, 9] have shown that in both cases at the phase transition order change concentration phase transformations are accompanied by anomalously large heat capacity discontinuities. In order to understand the

reasons of similarities and differences between these two rare-earth dihydrides ( $\text{LaH}_{2+c}$  and  $\text{CeH}_{2+c}$ ) we have to recall briefly some basic relations characterizing the thermodynamics of the hydrogen subsystem in these hydrides.

**General relations.** In a number of rare-earth dihydrides  $\text{RH}_{2+c}$  N metal atoms form a *fcc* lattice which contains N octahedral interstitial positions forming a *fcc* lattice as well. The spatially ordered distribution of N( $\text{H}_0$ ) hydrogen atoms ( $\text{H}_0$ -atoms) on the set of N octahedral interstitial positions is described by a single distribution function  $n(x, y, z)$  [2]:

$$n(x, y, z) = c + \eta_1 \gamma \exp[i 2\pi x] + 2\eta_2 \gamma \cos[\pi(x+2y)], \quad (1)$$

where  $n(x, y, z)$  is a probability that the octa-interstitial position with coordinates  $x, y, z$  is occupied by a  $\text{H}_0$ -atom,  $c$  is the concentration of  $\text{H}_0$ -atoms defined as  $c = [N(\text{H}_0)/N]$ ,  $\eta_1$  and  $\eta_2$  are order parameters, and  $\gamma$  is a normalizing constant (in our case  $\gamma = 0.25$ ).

Function (1) on the set of octa-positions obtains three different values:  $n(x, y, z) = n_1, n_2$  and  $n_3$ , where

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

It should be stressed that rigorous physical restrictions are imposed on the “sites occupation numbers”  $n_1$ ,  $n_2$  and  $n_3$ . Particularly,

$$0 \leq n_1, n_2, n_3 \leq 1. \quad (3)$$

Both order parameters,  $\eta_1$  and  $\eta_2$ , are restricted by the relations (2) and (3).

The free energy of the ordering hydrogen subsystem described by the distribution function (1) can be written as [2-5]

$$F(\eta_1, \eta_2) = E(\eta_1, \eta_2) - TS(\eta_1, \eta_2), \quad (4a)$$

$$E(\eta_1, \eta_2) = Nk_B 0.5 [V_0 c^2 + V_1 (\gamma \eta_1)^2 + 2 V_2 (\gamma \eta_2)^2], \quad (4b)$$

$$S(\eta_1, \eta_2) = -Nk_B \sum_{i=1,2,3} v_i [n_i \ln n_i + (1-n_i) \ln(1-n_i)]. \quad (4c)$$

Here  $V_0$ ,  $V_1$  and  $V_2$  are energy parameters (taken in temperature units). Their values can be estimated from experimental data;  $n_i$  ( $i = 1, 2, 3$ ) are determined by expressions (2), while  $v_i$  ( $i = 1, 2, 3$ ) are parts of  $N$  interstitial sites where the location probabilities of H<sub>0</sub>-atoms  $n(x, y, z)$  equal  $n_1$ ,  $n_2$  and  $n_3$ , respectively. In conditions of distribution function (1),  $v_1 = v_2 = 0.25$  and  $v_3 = 0.5$ . As  $(v_1 + v_2 + v_3) = 1$ , we have:  $(v_1 n_1 + v_2 n_2 + v_3 n_3) = c$ .

The values of order parameters associated with the extrema of the free-energy function  $F(\eta_1, \eta_2)$  are defined by a pair of conditions:  $[\partial F / \partial \eta_1] = 0$ ,  $[\partial F / \partial \eta_2] = 0$ , which for the given function (4) look like

$$\ln [n_1 n_2 (1-n_3) / (1-n_1) (1-n_2) n_3] = -V_1 \eta_1 / T, \quad (5a)$$

$$\ln [n_1 (1-n_2) / (1-n_1) n_2] = -V_2 \eta_2 / T. \quad (5b)$$

The type of extremal points (solutions of eqs. (5)) is determined by the sign of second derivatives of the free energy function (4) and the sign of determinant formed with these derivatives:

$$\begin{aligned} \partial^2 F / \partial \eta_1^2 &= Nk_B \gamma^2 \{V_1 + T \gamma \{[n_1(1-n_1)]^{-1} + \\ &+ [n_2(1-n_2)]^{-1} + 2[n_3(1-n_3)]^{-1}\}\}, \end{aligned} \quad (6a)$$

$$\begin{aligned} \partial^2 F / \partial \eta_2^2 &= 2Nk_B \gamma^2 \{V_2 + \\ &+ T 2\gamma \{[n_1(1-n_1)]^{-1} + [n_2(1-n_2)]^{-1}\}\}, \end{aligned} \quad (6b)$$

$$\partial^2 F / \partial \eta_1 \partial \eta_2 = 2Nk_B \gamma^2 \{T \gamma \{[n_1(1-n_1)]^{-1} - [n_2(1-n_2)]^{-1}\}\}. \quad (6c)$$

$$\Delta(\eta_1, \eta_2) = (\partial^2 F / \partial \eta_1^2) (\partial^2 F / \partial \eta_2^2) - (\partial^2 F / \partial \eta_1 \partial \eta_2)^2. \quad (7)$$

If  $\Delta > 0$  and  $(\partial^2 F / \partial \eta_1^2) > 0$ , then the extremum is a minimum. If  $\Delta > 0$  and  $(\partial^2 F / \partial \eta_1^2) < 0$ , then it is a maximum, and if  $\Delta < 0$ , then it is a saddle point.

The scenario of the ordering processes in the systems characterized by a pair of long-range-order parameters,  $\eta_1$  and  $\eta_2$ , depends on the concentration of the ordering particles  $c$ , and on the ratio of energy parameters

$V_1$  and  $V_2$ , defined as

$$p = V_2 / V_1. \quad (8)$$

Basing on the analysis of experimental data it was established [5] that

$$p(\text{CeH}_{2+c}) = 1.25 > 1, \quad p(\text{LaH}_{2+c}) = 0.7743 < 1. \quad (9)$$

All the above mentioned mathematical relations are equally applicable to both compounds: LaH<sub>2+c</sub> and CeH<sub>2+c</sub>. Within the frames of the developed model the difference between these two systems is provided exclusively by the qualitatively different values of the “main energy parameter”  $p$ .

**Formulation of the problem.** Previous investigations performed for LaH<sub>2+c</sub> and CeH<sub>2+c</sub> compounds [6-9] had shown that in both cases there exist two critical concentrations,  $c_0^{(1)} < 0.5$  and  $c_0^{(2)} > 0.5$ , at which the type of phase transitions is altered. As mentioned above, phase transformations (order-order, or disorder-order, respectively) are continuous at concentrations  $c_0^{(1)} < c < c_0^{(2)}$ , and become discontinuous outside of this region.

In [8] it was shown that in metal-hydrogen compounds of CeH<sub>2+c</sub> type (where  $p > 1$ ) critical concentrations  $c_0^{(1)}$  and  $c_0^{(2)}$  can be determined analytically. In particular, it was established that

$$c_0^{(1)}(p) = 0.5 \{1 - [(p-1)/3]^{1/2}\},$$

$$c_0^{(2)}(p) = 0.5 \{1 + [(p-1)/3]^{1/2}\}. \quad (10)$$

In the present article we attempt to formulate some mathematical conditions for determination of critical concentrations  $c_0(p)$  in metal-hydrogen compounds of LaH<sub>2+c</sub> type, i.e. in compounds with the main energy parameter  $p < 1$ .

**Mathematical consideration.** In hydrides with  $p < 1$  the ordering process begins with continuous formation of equilibrium states of the type  $(\eta_1 \neq 0, \eta_2 = 0)$  [4]. In this case the pair of equations (5) reduces to one equation

$$2 \ln [n_0 (1-n_3) / (1-n_0) n_3] = -V_1 \eta_1 / T, \quad (5a')$$

here  $n_3$  is determined by (2) and

$$n_0 = c + \gamma \eta_1. \quad (2')$$

From (5a') it follows that on the  $\eta_1$ -axis each point  $(\eta_1, 0)$  is an extremum at the corresponding temperature  $T(\eta_1)$ , nominated as “extremal temperature” and defined as

$$T(\eta_1) = -V_1 \eta_1 / 2 \ln [n_0 (1-n_3) / (1-n_0) n_3]. \quad (11)$$

To determine the type of extremal points on  $\eta_1$ -axis we have to modify respectively expressions (6)-(7):

$$\begin{aligned} [\partial^2 F / \partial \eta_1^2]_{\eta_2=0} &= Nk_B \gamma^2 \{V_1 + 0.5 T(\eta_1) \times \\ &\times ([n_0(1-n_0)]^{-1} + [n_3(1-n_3)]^{-1})\}. \end{aligned} \quad (12a)$$

$$[\partial^2 F / \partial \eta_2^2]_{\eta_2=0} = 2Nk_B \gamma^2 \{V_2 + T(\eta_1) [n_0(1-n_0)]^{-1}\} \quad (12b)$$

(the cross-derivative  $[\partial^2 F / \partial \eta_1 \partial \eta_2]_{\eta_2=0}$  is zero).

At lowest  $\eta_1$ -values both derivatives (12) are positive and the extremum  $(\eta_1, 0)$  is a minimum [4]. At temperature lowering and increasing of the equilibrium values of parameter  $\eta_1$  one of the derivatives becomes negative, while the second one remains positive. As a result, the extremum on the  $\eta_1$ -axis transforms into a saddle point, denoting an appearance of the order-order transformation  $(\eta_1, 0) \rightarrow (\eta_1, \eta_2)$  [4]. Numerical calculations [9] have shown that this transformation may be continuous, or discontinuous. We intend to analyze the specific interrelations between the values of the main energy parameter  $p$  and concentration  $c$ , as it is this pair of parameters that defines the type of  $(\eta_1, 0) \rightarrow (\eta_1, \eta_2)$  phase transition.

**Conditions for phase transition type change.** Let us first consider the disorder-order transformation in the system with  $p < 1$  at temperature  $T = T_{tr1}$ , which is determined by the equality [4]

$$T_{tr1} = -V_1 [c(1-c)]. \quad (15)$$

The corresponding extremum  $(\eta_1=0, \eta_2=0)$  is a minimum. At lowering temperatures it moves towards its limiting value (boundary point)  $\eta_1(\text{max})$  defined by one of conditions (3) (namely by the requirement  $n_3 \geq 0$ ). The latter gives

$$\eta_1(\text{max}) = c/\gamma. \quad (16)$$

The interval  $0 < \eta_1 < \eta_1(\text{max})$  contains a point  $\eta_1(d)$ , at which the high-temperature minimum transforms into a saddle point. This point is determined by the condition

$$\Delta(\eta_1(d), 0) = 0 \quad (17)$$

and is reached at the temperature  $T = T(\eta_1(d))$ .

As shown by direct numerical calculations [9], if the order-order transformation is continuous, then  $T_{tr2} = T(\eta_1(d))$ , and when it is discontinuous, then  $T_{tr2}$  is in the vicinity of  $T(\eta_1(d))$  and, which is significant,  $T_{tr2} > T(\eta_1(d))$ .

Condition (17) is realized at rising  $\eta_1$ -values due to the sign-change of the bracket in the expression (12b). Thus, one of the rigorous requirements for the occurrence of the order-order phase transition in the vicinity of the point  $(\eta_1(d); \eta_2(d) = 0)$  at temperature  $T \approx T(\eta_1(d))$  is

$$V_2 + T(\eta_1(d)) [n_0(d)(1-n_0(d))]^{-1} = 0. \quad (18)$$

The type of this phase transformation depends on the temperature  $T(\eta_1(i), \eta_2)$  which is associated with the nonzero solution of eqs. (5) ( $\eta_1 \neq 0, \eta_2 \neq 0$ ). If  $T(\eta_1(d), \eta_2) > T(\eta_1(d))$  then we suspect that the order-order transformation had occurred at the point  $\eta_1(T_{tr2}) < \eta_1(d)$ , at some higher temperature  $T(\eta_1(T_{tr2})) > T(\eta_1(d))$ . In this case we have to compare at equal temperatures the free energy

values of two extremal points: one, on the  $\eta_1$ -axis, and second, outside of it. In these conditions the order-order transition will be discontinuous, of the first order type, as we have a range of temperatures at which both minima, on the  $\eta_1$ -axis and outside of it, coexist. The order-order transformation will become continuous when  $T(\eta_1(d), \eta_2) \approx T(\eta_1(d))$ . The following relation can be used as an indicator of realization of this condition:

$$[\partial^2 F(\eta_1(d), \eta_2 \approx 0) / \partial \eta_2^2] \leq 0. \quad (19)$$

Thus, we obtain a second condition that determines the order-order transition type. We have to estimate the limiting value of expression (6b) at  $\eta_1 \rightarrow \eta_1(d)$  and  $\eta_2 \rightarrow 0$ , and to determine the sign of the obtained expression. As a result we arrive at the relation (18). Thus, if at the value  $\eta_1 = \eta_1(d)$  equation (18) is satisfied, then both above-mentioned conditions for the continuous order-order transition, (17) and (19), are satisfied as well.

By taking into account expressions (8) and (11) we can rewrite relation (18) as

$$V_1 \{p + [T(\eta_1(d)) / V_1] [n_0(d)(1-n_0(d))]^{-1}\} = 0. \quad (18')$$

As  $n_0(d) = (c + \gamma \eta_1(d))$ , and the values of  $\eta_1(d)$  are restricted by condition  $\Delta(\eta_1(d); 0) = 0$  (and vary for different concentrations), it becomes obvious that expression (18'), finally, contains a single variable – concentration  $c$ . Thus (18') can be considered as an equation which determines in the ordering systems with a given main energy parameter  $p$  the critical values of concentrations  $c_0(p)$  at which the order-order transformation changes its type: within the concentration range  $0 < c < 0.5$  this transition is discontinuous for  $c < c_0(p)$ , and becomes continuous for  $c \geq c_0(p)$ .

**Approximate solution of equation (18').** The Figure presents  $T(\eta_1)$  dependences calculated using expression (11) for compounds  $\text{LaH}_{2+c}$  ( $p = 0.7743$ ;  $c = 0.05, 0.10, 0.15, 0.20, 0.25$  and  $0.30$ ). The specific points at which  $\Delta(\eta_1, 0)$  changes its sign are denoted by triangles. These numerical results indicate that differences between temperatures  $T(\Delta = 0)$  and  $T_{tr1} \equiv T(\eta_1 = 0)$  are about 10%. This detail allows us (in order to approximate estimation of  $c_0(p)$  dependence) to replace  $T(\eta_1(d))$  by  $T_{tr1}$  in (18'). Then, using expression (15), we obtain the equation:

$$p - [c(1-c)] / [n_0(d)(1-n_0(d))] = 0. \quad (18'')$$

The next crude approximation consists in the replacement of  $n_0(d) \equiv n_0(\eta_1(d))$  by its limiting value  $n_0(\eta_1(\text{max}))$ , where  $\eta_1(\text{max})$  is determined by (16) which yields  $n_0(\eta_1(\text{max})) = 2c$ . It follows that

$$n_0(d) [1 - n_0(d)] \approx 2c(1 - 2c).$$

Within the frames of this additional crude approximation equation (18'') will take the following simple form:

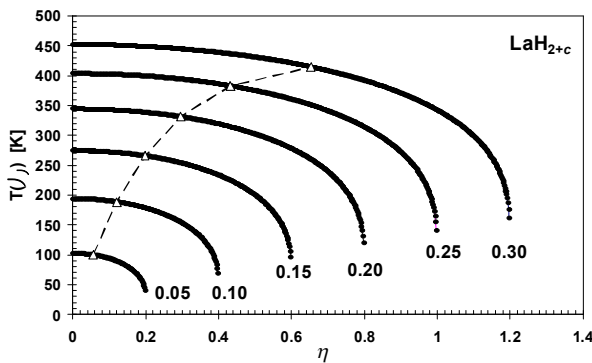


Fig. Temperatures  $T(\eta_1)$  associated with the partially ordered states ( $\eta_1 \neq 0, \eta_2 = 0$ ) located on  $\eta_1$ -axis. Triangles denote the specific  $T(\eta_1)$ -values associated with the points  $(\eta_1(d), 0)$  at which  $\Delta(\eta_1(d), 0) = 0$  and the free-energy extremum  $(\eta_1, 0)$  changes its type.

$$2p - [(1 - c) / (1 - 2c)] = 0. \tag{19}$$

On solving it with respect to  $c$ , we obtain

$$c_0(p) = (2p - 1) / (4p - 1). \tag{20}$$

As  $p(\text{LaH}_{2+c}) \approx 0.75$ , for the critical concentration  $c_0(p)$  the latter expression gives

$$c_0(p)[\text{LaH}_{2+c}] = 0.25 \tag{21a}$$

that is in good agreement with our results of precise numerical calculations [9].

**Brief conclusions.** In spite of the above-mentioned coincidence of data provided by expression (20) with the results of direct numerical calculations [9], this oversimplified dependence has to be treated very carefully. Particularly, from (20) it follows that  $c_0(p = 0.5) = 0, c_0(p < 0.5) < 0$ , and, finally, for  $p = 0.25$  we have  $c_0(p = 0.25) = \infty$ .

On the other hand, for  $p = 1.25$  expression (20) gives

$$c_0(p) = 0.375 \tag{21b}$$

that is in good agreement with the results of direct numerical calculations [8] which are performed for  $\text{CeH}_{2+c}$  compounds (in condition that  $p(\text{CeH}_{2+c}) = 1.25$ ) and establish the existence of a tricritical point (the phase transition type change point) at concentration  $c \approx 0.36$ .

It means that in the physically meaningful range of energy parameter  $p$  expression (20) represents the  $c_0(p)$  dependence qualitatively well, and that it can be used for qualitative estimations of specific concentrations  $c_0$  characterized by anomalously large heat capacity discontinuities at the phase transition points. For more precise determination of  $c_0(p)$  values the system of equations (11) and (18') has to be solved numerically.

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ფიზიკა

ფაზური გადასვლის გვარობის შეცვლის წერტილის განსაზღვრა LaH<sub>2+c</sub>-ტიპის მოწესრიგებად დიჰიდრიდებში

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(წარმოდგენილია აკადემიის წევრის გ. ჯაფარიძის მიერ)

ნაშრომში განიხილება იშვიათ მიწათა მოწესრიგებადი წყალბადნაერთები RH<sub>2+c</sub> (0 < c < 0.5), რომლებშიც წყალბადის მოწესრიგებული განლაგება ლითონის მესერის კვანძთაშორის პოზიციებში ხასიათდება წესრიგის ორი პარამეტრით ( $\eta_1$  და  $\eta_2$ ). წინა შრომებში სითბოტევადობის რიცხვითი გამოთვლები ჩატარებული გვეჩვენა RH<sub>2+c</sub> დიჰიდრიდების ორი კლასისათვის. ერთს ვუწოდეთ CeH<sub>2+c</sub> ტიპის ნაერთები (აქ ენერგეტიკული

პარამეტრი  $p$  აღემატება ერთს ( $p > 1$ ) და უწესრიგობა-წესრიგის გადასვლის დროს წარმოიქმნება მდგომარეობა ( $\eta_1 \neq 0, \eta_2 \neq 0$ ), ხოლო მეორეს -  $\text{LaH}_{2+c}$  ტიპის ნაერთები (აქ ენერგეტიკული პარამეტრი  $p$  ნაკლებია ერთზე ( $p < 1$ ), უწვევტი უწესრიგობა-წესრიგის გადასვლისას წარმოიქმნება მდგომარეობა ( $\eta_1 \neq 0, \eta_2 = 0$ ), და მხოლოდ უფრო დაბალ ტემპერატურებზე, წესრიგი-წესრიგის ტიპის გადასვლის შედეგად ვლდებულობთ მდგომარეობას ( $\eta_1 \neq 0, \eta_2 \neq 0$ ). ეს უკანასკნელი გადასვლა წყალბადის შედარებით დაბალ კონცენტრაციებზე ( $c < c_0$ ) ხორციელდება ნახტომისებურად (I გვარის ფაზური გადასვლის მსგავსად), ხოლო კონცენტრაციის გაზრდისას (შუალედში  $c_0 < c < 0.5$ ) ის უწვევტ ხასიათს ღებულობს (II გვარის ფაზური გადასვლის მსგავსია). კრიტიკულ კონცენტრაციაზე  $c_0$ , სადაც ხდება ფაზური გადასვლის გვარობის შეცვლა, წესრიგი-წესრიგის გადასვლასთან დაკავშირებული სითბოტევადობის პიკი ანომალურად ღიდი ხდება.

ამჟამად ჩვენ განვიხილეთ მოწესრიგებადი სისტემები, სადაც  $p < 1$  და გავანალიზეთ ის თანაფარდობები, რომლებიც განსაზღვრავენ კონცენტრაციის კრიტიკულ მნიშვნელობას  $c_0$ . მიღებულია მიაზლოებითი ფორმულა  $c_0$ -ის დამოკიდებულებისა მოწესრიგებადი ქვესისტემის ენერგეტიკულ პარამეტრზე  $p$ , რაც საშუალებას გვაძლევს შევაფასოთ მოცემული ნაერთის ის კონცენტრაცია, რომლის დროსაც წესრიგი-წესრიგის ტიპის ფაზური გადასვლის წერტილში სითბოტევადობის ნახტომი ანომალურად ღიდი ხდება. მიღებული ფორმულა თვისობრივად სწორად აღწერს რეალურ წყალბადნაერთებს.

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