

Physics

Ordering Effects in the Heat Capacity of Light Rare-Earth Superstoichiometric Dihydrides. $CeH_{2.86}$

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ABSTRACT. CeH_{2+c} -type ordering hydrides are considered. Different ingredients of the total heat capacity $C(T)$ of these ordering interstitial alloys are calculated and the summary result is compared with the corresponding experimental data.

Metal-hydrogen interstitial alloys (M-H compounds) are considered usually as consisting of thermodynamically sufficiently independent following main subsystems: the lattice of metal atoms, the set of interstitial light atoms located in tetrahedral interstitial positions (tetra-positions) and octahedral interstitial positions (octa-positions), and the system of conduction electrons. It has to be taken into account that in superstoichiometric rare-earth dihydrides the subsystem of additional light atoms distributed on the set of octa-positions reveals a tendency to form ordered spatial configurations, which is associated with corresponding changes of the internal energy of light atoms. Generally, in rare-earth hydrides we have to consider as well the subsystem of local magnetic moments associated with metal ions, but in the hydrogen-rich cerium hydride magnetic interactions in the lattice we assume to be negligibly small. In such conditions the measured heat capacity $C(T)$ of the given M-H compound consists of the following main components: *a*) heat capacity caused by acoustic waves in the metal lattice, *b*) heat capacity caused by local vibrations of light interstitial atoms in tetra- and octa-interstitial positions (characterized by different local frequencies), *c*) heat capacity related to the ordering processes in the subsystem of octa-hydrogen atoms, and *d*) heat capacity induced by conduction electrons.

Basing on the standard mathematic expressions for the heat capacity ingredients mentioned above and using the set of energy constants defined in our previous article, an excellent coincidence between the calculated and measured $C(T)$ dependencies is obtained in a wide temperature range. © 2012 Bull. Georg. Natl. Acad. Sci.

Key words: rare-earth hydrides, ordering processes, ingredients of the total heat capacity.

Introduction. The ordering superstoichiometric rare-earth dihydrides were widely investigated during the 1960s-1990s. Careful measurements were made and the most significant results were summarized in a number of reviews (see e.g. [1]). Some attempts were made as well to describe the observed temperature

dependences of characteristic physical properties and, finally, to understand the nature of hydrogen-metal bonding in different metal-hydrogen compounds. In all cases it was assumed that in “heavy metal” – hydrogen alloys (M-H alloys) H-atoms occupy interstitial positions of the given symmetry and that at low

temperatures they form some spatially ordered configurations (if their number is less than the number of corresponding interstitial positions). Thus, we usually consider the M-H compounds as consisting of some, thermodynamically sufficiently independent, subsystems: metal lattice, the set of interstitial light atoms, and the system of conduction electrons. We assume additionally that even if metal ions possess some local magnetic moments, magnetic ordering in the lattice is absent (i.e. magnetic interactions in the lattice can be neglected). In such conditions the measured heat capacity $C(T)$ of a given M-H compound can be considered to contain the following ingredients: that induced by the acoustic waves in the lattice of N metal atoms (denoted as $C_{ac}(T)$), that induced by the local vibrations of N_H light interstitial atoms (denoted generally as $C_{ord}(T)$), that related to the ordering processes (denoted as $C_{ord}(T)$), and that induced by conduction electrons (denoted as $C_{ac}(T)$),

It should be stressed that in the case of cerium hydrides (as well as in lanthanum hydrides) even a small number N_H of H-atoms embedded in the *hcp*-lattice of N metal atoms ($N_H \ll N$) form local “islands” of dihydrides MH_2 with a *fcc* metal lattice where H-atoms occupy preferentially tetrahedral interstitial positions. For compounds MH_{2+c} ($0 < c < 1$) it was established that N metal atoms form a *fcc* lattice, where $2N$ H-atoms occupy $2N$ tetrahedral interstitial positions (they are called “ H_T -atoms”), while additional cN H-atoms (called respectively “ H_O -atoms”) are distributed among N octahedral interstitial positions and at low temperatures form spatially ordered superstructures described by two long-range-order (LRO) parameters, η_1 and η_2 . Correspondingly, we have to distinguish local vibrations of H_T -atoms and H_O -atoms, as their bonds with surrounding metal atoms are presumably different.

In our previous article [2] we considered quasi-stoichiometric dihydrides of rare-earth metals and adjusted the numerical values of characteristic parameters describing the heat capacities of different subsystems in metal-hydrogen compounds – the Debye characteristic temperature T_{Deb} (for acoustic vibrations of metal lattice), Einstein characteristic

temperature T_E (for local vibrations of H-atoms located in tetrahedral sites of *fcc* metal lattice), and factor g (characterizing the electronic specific heat). Some basic mathematical relations were also presented for calculations of specific heat ingredients – $C_{ac}(T)$, $C_{op}(T)$ and $C_{el}(T)$. We shall not repeat these expressions here, and concentrate our attention on the additional ingredients of the total heat capacity in compounds MH_x ($x > 2$) induced by the set of H_O -atoms. These are the heat capacity associated with local vibrations of H_O -atoms in the ordered and disordered spatial configurations $C_{op}(H_O)$, and the heat capacity of the ordering process $C_{ord}(T)$.

Formulation of the problem. In [3] the results of low temperature heat capacity measurements taken on cerium hydride $CeH_{2.86}$ were presented, where the influence of hydrogen ordering on the temperature dependence of the total heat capacity was clearly registered. *We intend to calculate temperature dependent heat capacity of this compound, basing on the symmetry properties of the free energy function of ordering subsystem established in [4], due to which the hydrogen vacancies ordering process in $CeH_{2.86}$ can be described as the ordering of H_O -atoms in the compound $CeH_{2.14}$.*

Heat capacity of the ordering process in a system characterized by two LRO parameters. This problem was widely considered in a number of our previous articles and we shall give below only a brief summary of the main mathematical relations.

Ordering of a binary A-B alloy implies that different sites of a given crystalline lattice are characterized by different occupation probabilities of A and B components. In case of the ordering hydrogen subsystem the roles of A and B atoms are played, respectively, by H-atoms and their vacancies. It was established [5] that in superstoichiometric cerium dihydrides CeH_{2+c} the ordering of H-atoms located in octahedral positions (H_O -atoms) is characterized by two LRO-parameters $\eta_1(T)$ and $\eta_2(T)$, which provide existence of three different occupation probabilities (of octahedral interstitial positions) - n_1 , n_2 and n_3 :

$$\begin{aligned} n_1 &= c + \eta_1\gamma + 2\eta_2\gamma, & n_2 &= c + \eta_1\gamma + 2\eta_2\gamma, \\ n_3 &= c - \eta_1\gamma \end{aligned} \quad (1)$$

($\gamma = 0.25$ is a normalizing factor).

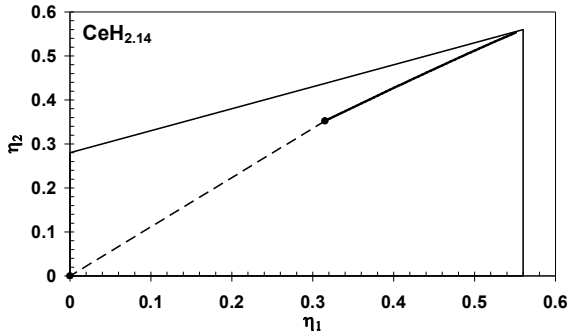


Fig. 1a. Trajectory of the ordering process in (η_1, η_2) space.

Equilibrium values of the order parameters η_1 and η_2 are determined from equations [5]

$$\ln \left[\frac{n_1 n_2 (1-n_3)^2}{(1-n_1)(1-n_2) n_3^2} \right] = -(V_1/T) \eta_1 \quad (2a)$$

$$\ln \left[\frac{n_1 (1-n_2)}{n_2 (1-n_1)} \right] = -(V_2/T) \eta_2 \quad (2b)$$

which can be solved only numerically (V_1 and V_2 are Fourier-components of H_O - H_O interaction potential taken in temperature units; they can be estimated from experimental data).

The main energy parameter of the ordering subsystem is the ratio $p = [V_2 / V_1]$. In the case of CeH_x compounds $p > 1$; particularly, $p[CeH_x] = 1.25$ [5].

The ordering subsystem of H_O -atoms is characterized by the ordering energy [5]

$$E_{ord}(\eta_1, \eta_2) = Nk_B 0.5 [V_1 (\gamma \eta_1)^2 + 2V_2 (\gamma \eta_2)^2], \quad (3)$$

which is zero in the disordered state and reaches its lowest value at maximum order.

Heat capacity of the ordering subsystem is determined as temperature derivative of the function $E_{ord}(\eta_1, \eta_2)$:

$$C_{ord}(T) = dE_{ord}(\eta_1, \eta_2) / dT \quad (4)$$

Numerical results for the ordering subsystem in the model compound $CeH_{2.14}$. It is known [1] that in the given compound $2N$ tetrahedral interstitial positions are filled by $2N H_T$ -atoms, while concentration of H_O -atoms c equals $c = 0.14$. It can be estimated [4] that in cerium dihydrides for concentration $c = 0.14$ the energy parameters of the ordering subsystem V_1 and V_2 are as follows:

$$V_1[CeH_{2.14}] = -1540 \text{ K}, V_2[CeH_{2.14}] = -1925 \text{ K}. \quad (5)$$

Solution of equations (2) gives us a detailed description of the ordering process presented in Figs

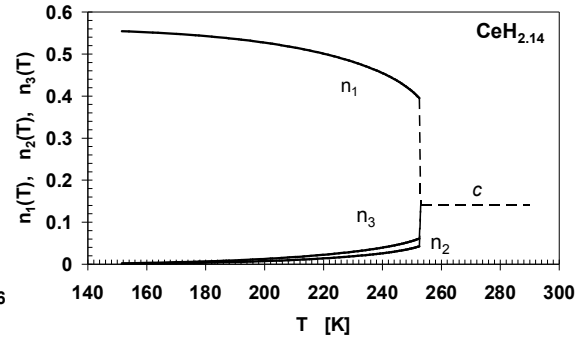


Fig. 1b. Temperature dependence of occupation numbers

1a and 1b, showing, particularly, the trajectory of the ordering process in the space of order parameters η_1 and η_2 (Fig. 1a), and temperature dependence of occupation numbers $n_1(T)$, $n_2(T)$ and $n_3(T)$ (Fig. 1b). (“Trajectory of the ordering process” is the sequence of points in the (η_1, η_2) -space denoting the set of equilibrium states at gradually varying temperature).

The ordering energy (3) and its temperature derivative (4) are given in Figs. 2a and 2b, respectively.

Numerical results for the heat capacity of compound $CeH_{2.86}$. Using the mathematical scheme already applied to the heat capacity calculations in quasi-stoichiometric lanthanum dihydride LaH_2 [2] (where all hydrogen atoms were assumed to be located exclusively in the tetrahedral interstitial positions) and adding the heat capacity parts associated with vibrations of “superstoichiometric” H_O -atoms and with ordering of these H_O -atoms, we arrive at the following summary expression:

$$C(T) [CeH_{2.86}] = C_{ac}(M) + C_{op}(H_T) + C_{op}(H_O) + C_{ord}(H_O) + C_{el}, \quad (6)$$

where the first, second and last term (metal lattice acoustic waves, vibrations of H_T -atoms and electronic specific heat) were already considered in [2], while the third and fourth terms will be considered below.

As mentioned above, equations (2) can be solved only numerically and consequently analytical temperature dependences cannot be obtained either of the energy function (3), or of its derivative (4). Numerical dependence $C_{ord}(H_O)$ is given in Fig. 2b, on assuming that concentration of the ordering component equals $c = 0.14$.

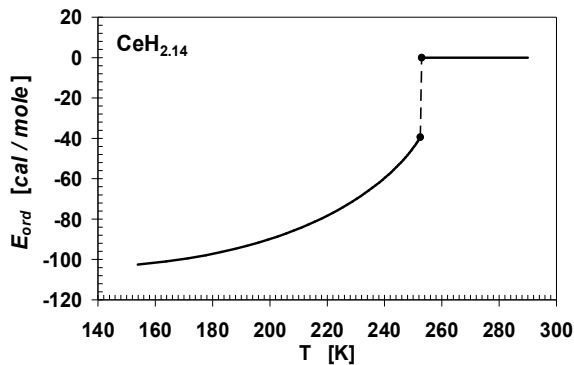


Fig. 2a. Temperature dependence of equilibrium energy of the ordering subsystem.

The heat capacity related to local vibrations of H_o -atoms is proportional to the number of oscillating particles, and thus, we imply that in this case $c = 0.86$.

A few words about the electronic term which is presented usually as $C_{el}(T) = g T$, where g depends on the number of mobile electrons (or on the density of states at the Fermi level). It was established that during the hydrogenation process hydrogen atoms introduced in the lattice of rare-earth metals capture itinerant electrons of metal lattice and deplete gradually the conduction band [6]. In order to take this effect into account we have used the “reduced value” of factor g (determined experimentally for pure dihydride and used in [2]) on applying the relation: $g[\text{CeH}_{2+c}] = (1 - c) g[\text{CeH}_2]$. (7)

Proceeding from physical reasons we have selected the following set of parameters characterizing the metal-hydrogen system investigated in [3]:

$$T_{\text{Deb}} = 140 \text{ K}, T_{\text{Ein}}(\text{tetra}) = 1240 \text{ K}, T_{\text{Ein}}(\text{octa}) = 744 \text{ K}, \\ g = 0.00028 \text{ (cal / mole K}^2\text{)}. \quad (8)$$

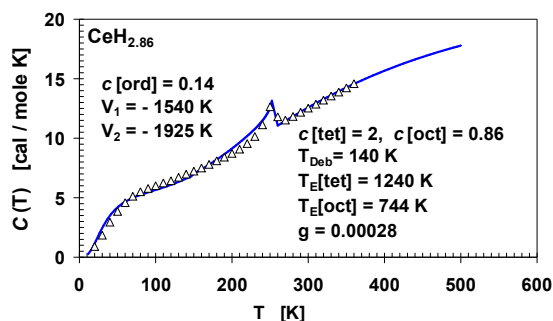


Fig. 3. Temperature dependence of the heat capacity of $\text{CeH}_{2.86}$. The sequence of triangles – experimental data [3], full line – calculated $C(T)$ curve. The numerical values of the characteristic parameters are indicated in the figure.

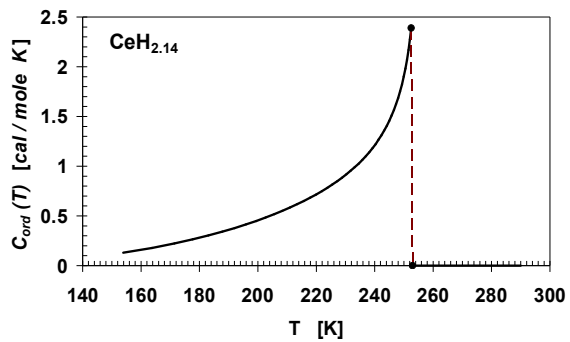


Fig. 2b. Heat capacity of the ordering subsystem.

The results of calculations based on parameters (5) and (8) are presented in Fig.3 together with experimental points [3]. We see that general experimental $C(T)$ dependence in a wide temperature range is successfully represented by the calculated curve.

Brief comments. Agreement between the theoretical and experimental data is excellent, but there arise some doubts. We have not taken into account the hydrogen “weighting” effect induced by ordering processes [7]. Our attempts to modify parameter $T_{\text{Ein}}(\text{octa})$ and to make it temperature dependent (as in the case of deuteride V_2D [7]) gave a negative result – modified $C(T)$ -curve became separated from experimental points. This apparent “anomaly” has to be considered in the future. (Perhaps the mobility of massless vacancies of H_o -atoms in the ordering $\text{CeH}_{2.86}$ is qualitatively different from the mobility of H_o -atoms in the ordering $\text{CeH}_{2.14}$).

Conclusions. In spite of the used crude assumptions the selected set of energy parameters (5) and (8) enable us to give an adequate description of the heat capacity temperature dependence of the given metal-hydrogen compound. Parameters (8) are slightly different from those used in [2], and this is a strong stimulus for further investigations aimed to understand the physical reasons of variations of the mentioned parameters induced by variations of hydrogen concentration.

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