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Physics

Heat Capacity of Rare-Earth Quasi-Stoichiometric Dihydrides

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(Presented by Academy Member George Japaridze)

ABSTRACT. Temperature dependence of the total heat capacity of light rare-earth dihydrides is calculated. The results of calculations are compared with the corresponding experimental data and a number of parameters characterizing the metal-hydrogen system are determined. *© 2011 Bull. Georg. Natl. Acad. Sci.*

***Key words**: rare-earth hydrides; heat capacity; lattice vibrations.*

It is well known that the great majority of rare-earth metals are characterized by a hexagonal crystal lattice. In the case of "light rare-earths" (from lanthanum to neodymium) the sequence of "hexagonal atomic plates" looks like ABACABAC etc., while in "heavy rare-earths" (from gadolinium to lutetium, and additionally in scandium and yttrium) metal lattice contains the sequence of hexagonal plates of the type ABABAB etc. In both cases hydrogen atoms are easily absorbed by the metal lattices, but the behavior of absorbed H-atoms is different. In "heavy rare-earths" at the beginning of the hydrogenation process H-atoms are dissolved in the hexagonal metal lattice and form solid solutions (α-phase) up to some specific maximal concentration $x_{max}(a)$. At hydrogen concentrations $x > x_{max}(\alpha)$ a biphase state is formed: one of the phases is the hexagonal α-solid solution RH_x ($x = x_{max}(\alpha)$) and the other is a β-phase - a dihydride RH_2 characterized by the *fcc* metal lattice where hydrogen atoms are located in the tetrahedral interstitial positions. In the "light rare-earth" hydrides the hexagonal solid solution α-phase is absent and even at the lowest summary hydrogen concentrations x "islands" of *fcc* dihydrides RH_2 are formed in the "sea" of hexagonal metal lattice. In the case of a pure β-phase N metal atoms form a *fcc* lattice containing 2N tetrahedral interstitial positions and N octahedral positions. It was established [1] that at hydrogen concentration $x = 2$ in the "light rare-earth" dihydrides RH_2 the set of 2N tetrahedral interstitial positions is filled with 2N hydrogen atoms, while the octa-interstitial positions remain empty.

In a series of experimental investigations (see e.g. [2-4]), the low-temperature heat capacities of mono-phase lanthanum and cerium dihydrides RH_2 were measured. It was assumed that all absorbed H-atoms were located exclusively in the tetrahedral interstitial positions of the *fcc* metal lattice. We intend to calculate the heat capacity of such a metal-hydrogen system under the same conditions.

Main components of the heat capacity of metal hydrides. H-atoms inserted in the host metal lattice alter its heat capacity**.** First of all, the set of inserted H-atoms changes the interatomic distances between the metal atoms and in this way change the spectrum of acoustic modes of the metal lattice. On the other hand, there arises a heat capacity part associated with the local vibrations of H-atoms in the interstitial positions. And, finally, as hydrogen atoms capture a part of conduction electrons, they reduce the number of free carriers and change the electronic part in the total heat capacity of the metal-hy-

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drogen compound. As in the case of an ideal rare-earth dihydride RH_2 it is assumed that hydrogen atoms fill all existing tetrahedral positions and all octa-positions remain empty, the ordering processes are excluded and the corresponding part of heat capacity is absent.

Basic relations [5]. We assume that N metal atoms located at the sites of a *fcc* lattice take part in the acoustic waves characterized by the Debye spectrum with the limiting frequency ν_M, while $2N$ hydrogen atoms located in $2N$ tetrahedral interstitial positions oscillate with a single Einstein frequency ν_E. We assume as well that thermally activated conduction electrons are characterized by the density of states at the Fermi surface $n(E_F)$.

On assuming that each quantum oscillator of frequency ν at temperature T has a Planck mean energy

$$\varepsilon_n = h\nu\,[exp(h\nu/kT) - 1]^{-1} \qquad (1)$$

the heat capacity part, associated with the local vibrations of $2N$ hydrogen atoms in 1 mole of RH_2 compound (containing N metal atoms) is described by the Einstein relation:

$$C_E(T) = 6R_0\,[z_E(T)]^2\,\{exp(z_E(T))/(exp(z_E(T)) - 1)^2\}, \qquad (2)$$

where

$$z_E(T) \equiv h\nu_E/kT. \qquad (3)$$

In a number of published articles instead of local mode frequencies ν_E the corresponding Einstein's temperatures T_E are usually indicated. T_E is determined as:

$$T_E \equiv h\nu_E/k. \qquad (4)$$

Thus, $z_E(T)$ can be presented as a ratio:

$$z_E(T) \equiv T_E/T. \qquad (3')$$

In order to describe the metal lattice heat capacity within the frame of Debye approximation we introduce a set of following notations:

$$z_M(T) \equiv h\nu_M/kT, \quad T_D \equiv h\nu_M/k, \quad z_M(T) \equiv T_D/T, \qquad (5)$$

where ν_M is the limiting frequency of Debye spectrum.

Then, for the given simplified spectrum of lattice vibrations, the heat capacity associated with the acoustic waves in 1 mole of RH_2 compound can be presented as

$$C_D(T) = 9R_0 D(T)\cdot$$

$$D(T) = \left(\frac{T}{T_D}\right)^3 \int_0^{z_M} \left\{\left[z(T)\right]^4 \exp(z(T))/(\exp(z(T)) - 1)^2\right\} dz, \qquad (6)$$

Thus, the "lattice part" of the heat capacity of RH_2 compounds can be written as

$$C_{lat}(T) = C_D(T) + C_E(T), \qquad (7)$$

where $C_D(T)$ and $C_E(T)$ are given by expressions (2) and (6), and R_0 (the gas constant) is equal to 8.31441 J/mole K (1.98714 cal / mole K).

To calculate the electronic heat capacity the following expression is usually used:

$$C_{el}(T) = gT, \qquad (8)$$

where the factor g is proportional to the density of electronic states at the Fermi-level $n(E_F)$.

Summarizing the above brief consideration we conclude that basing on relations (2), (6) and (8) the experimentally measured molar heat capacities of RH_2 compounds can be represented by the expression

$$C(T) = C_{lat}(T) + C_{el}(T) \qquad (9)$$

in conditions of suitably selected parameters T_E, T_D and g.

Results of numerical calculations. Characteristic parameters T_D and g for dihydride LaH_2 were determined in [3] where the $C(T)$ dependence was measured in the temperature range (1-20)K. They were compared with the corresponding values obtained previously for pure lanthanum metal. Both sets of numerical data are shown below in a short Table, where are also presented our selected values of T_E, T_D and g parameters (see the last row), obtained at satisfying the experimental $C(T)$ curve [4] at (1-350)K.

In Fig. 1 we present the results of our numerical calculations based on expressions (2)-(9) and the set of selected parameters. The corresponding experimental points [4] are denoted by circles. It is interesting to note that there exists a significant deviation between the experimental and calculated points in the temperature range 150-250K. This deviation is shown more precisely in Fig. 2, where the difference $\Delta C(T) \equiv C(T)$[measured] - $C(T)$[calculated] is presented.

Brief comments. The selected parameter values – T_D, T_E and g - provide an excellent description of the ex-

Table 1

Compound	T_D (K)	T_E (K)	g (cal/mole K^2)
La	151	--	0.00227
LaH_2 (1-10) K	243	(?)	0.00204
LaH_2 (1-350) K	210	1200	0.00204

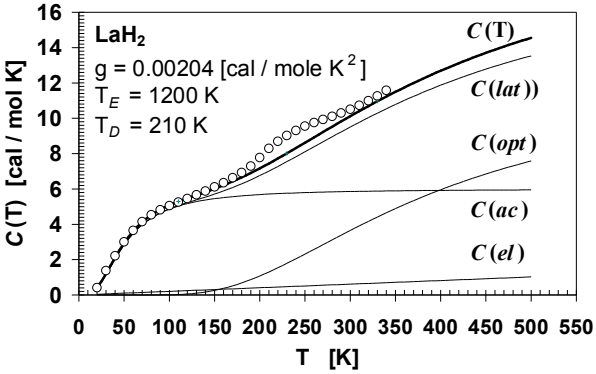

Fig. 1. The measured (circles) and calculated (thick line) total heat capacity of LaH_2; thin lines denote the components of calculated heat capacity: $C(el) \equiv C_{el}(T)$, $C(ac) \equiv C_{ac}(T)$, $C(opt) \equiv C_{opt}(T)$, $C(lat) \equiv C_{lat}(T) = C(ac) + C(opt)$.

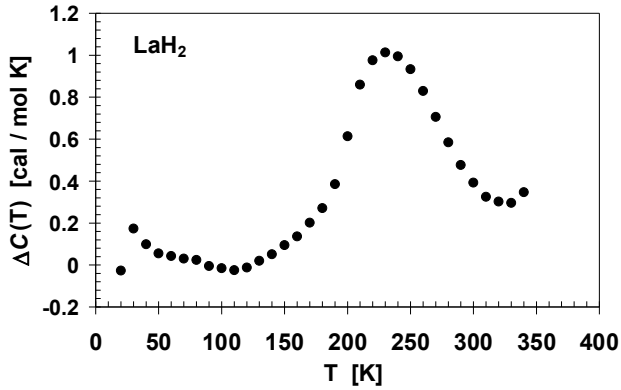

Fig. 2. Difference between the measured and calculated heat capacity values.

perimentally established C(T) dependence. On comparing the used numerical values of T_D and g parameters with the data determined in the earlier measurements we conclude that both parameters are physically reasonable. Particularly, variations of Debye temperature T_D (see Table 1) can be explained by variations of the metal lattice stiffness induced by two factors - by the interstitial hydrogen atoms and by variations of temperature. It is well known that due to the inserted H-atoms metal-metal indirect bonds become stronger, which provides, on the one hand, a significant contraction of metal lattices in rare-earth hydrides [1] and, on the other, induces an increase of the acoustic mode frequencies revealed at increasing the Debye temperature from 150K in pure lanthanum to 243K in its dihydride [3]. It is known as well that the "Debye temperature" lowers at lattice heating (due to the effective softening of interatomic bonds). This is the reason why the value of T_D determined at $T \leq 10$K ($T_D = 243$K) is sufficiently higher than that determined in the temperature range up to 350K ($T_D = 210$K).

Now about the decrease of the electronic heat capacity constant g at the development of the hydrogenation process (see Table 1). This phenomenon is easily explained with account of the well-known gradual depleting of the conduction electron band by the inserted hydrogen atoms, and corresponding decrease of the number of charge carriers.

A few words concerning the difference between the calculated $C(T)$ dependence and the experimental points shown in Fig. 2. There can be different reasons for this deviation.

One of the usually considered versions involves the assumption that a number of H-atoms which have to be located in tetrahedral positions (H_t-atoms) are transferred into the octahedral positions. It means that in equilibrium $2N$ tetrahedral positions are occupied not by $2N$ H-atoms, but only by $(2 - c)N$ H_t-atoms, while the remaining part of H-atoms - cN H_O-atoms – fill a part of N octahedral positions. Within the frame of this model we have to assume additionally that the set of H_O-atoms undergoes an order-disorder transition at some temperature T_{tr} [6]. If the concentration of H_O-atoms is of the order of $c \approx 0.1$–0.15, then, following [6], $T_{tr}(c)$ will become very close to the temperature of the heat capacity anomaly shown in Fig. 2 (~ 230K). It follows that this anomaly is related to the order-disorder transition in the subsystem of H_O –atoms.

The next model to be discussed is based upon the assumption that all H_t-atoms remain in their tetrahedral positions, but interactions existing between these particles are so strong that there are formed acoustic waves which propagate exclusively in the subsystem of H_t-atoms. The additional heat capacity is ascribed to these specific acoustic waves.

There exists as well a third mechanism of hydrogen subsystem excitation. If we assume that compounds of the type of LaH_2 consist of the metal-hydrogen complexes MH_2 [7], then we have to consider the possibility of their individual or collective rotational motions, which will be responsible for the additional energy absorption in the suitable temperature range.

All the above-mentioned processes are more or less acceptable from the physical point of view and need to be verified numerically in the future.

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ფიზიკა

იშვიათ-მიწათა კვაზისტექიომეტრიული დიჰიდრიდების სითბოტევადობა

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ნაშრომში განიხილება იშვიათ-მიწათა კვაზისტექიომეტრიული წყალბადნაერთები RH_x ($x \approx 2$). იგულისხმება, რომ წყალბადის ატომები განლაგებულია ტეტრაედრული ტიპის კვანძთაშორის პოზიციებში. LaH_2 დიჰიდრიდის მაგალითზე გამოთვლილია ასეთი ტიპის ნაერთების სრული სითბოტევადობა ტემპერატურის ფართო დიაპაზონში. გამოთვლის შედეგები შედარებულია შესაბამის ექსპერიმენტულ მონაცემებთან და ამის საფუძველზე დადგენილია მოცემული სისტემის მახასიათებელი პარამეტრების რიცხვითი მნიშვნელობანი: T_D - აკუსტიკური რხევების მახასიათებელი დებაის ტემპერატურა, T_E - ოპტიკური რხევების მახასიათებელი აინშტაინის ტემპერატურა, და g - ელექტრონული სითბოტევადობის კონსტანტა. თეორიული და ექსპერიმენტული მრუდების საერთო კარგი თანხვედრის ფონზე გამოვლენილია დამატებითი პროცესი, რომელსაც წვლილი შეაქვს განხილული ნაერთის ჯამურ სითბოტევადობაში. გამოთქმულია გარკვეული მოსაზრებები ამ დამატებითი პროცესის საკარაუდო ბუნების შესახებ.

REFERENCES

1. *P. Vajda* (1995), in: Handbook on the Physics and Chemistry of Rare-Earths (Eds. K.A.Gschneidner, L.R.Eyring), North-Holland, v. **20**, p. 209-294.
2. *B. Stalinski, Z. Bieganski* (1964), Bull. Acad. Pol. Ser. Chem., **12**, 5: 331-334.
3. *Z. Bieganski, D. Gonzalez Alvarez, F.W. Klaijsen* (1967), Physica (Utrecht), **37**: 153-157.
4. *Z. Bieganski* (1971), Bull. Acad. Pol. Ser. Chem., **19**, 9: 581-586.
5. *P.H. Keesom and N. Pearlman* (1954). in: Handbuch der Physik (ed. S.Flugge), Springer, v. XIV, pp. 282-337.
6. *I.G. Ratishvili, P. Vajda* (1997), Journ. of Alloys and Compounds, **253-254**: 171-174.
7. *N.Z. Namoradze, I.G. Ratishvili* (2008), in: Carbon Nanomaterials in Clean Energy Hydrogen Systems (Eds. B. Baranowski et al.), Springer, 549-572.

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