CORRELATION BETWEEN ELASTIC- AND THERMODYNAMIC PROPERTIES AND ELECTRONIC PARAMETERS OF RARE-EARTH METAL HYDRIDES

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Introduction

A fabrication of pure rare-earth metals (REM) from pure oxides by their intensive hydrogenation at 700-900 ^{0}C is known [1-2]. The thermodynamics data of REM-hydrides are necessary for optimization of this process. Therefore this work deals with the issue.

Results and discussion

The analysis of link of thermodynamic properties with results of calculation of an electronic spectrum in system REM – hydrogen has been carried out.

Calculation was carried out by a method of group orbits of linear combination atomic orbits (GOLCAO) [3]. Calculated for one of hydrides, the spectrum is resulted in table 1.

Dissociation energy (E_a) of investigated objects was calculated too. The analysis of elastic and thermodynamics state was carried out. The elastic module of all-round compression (β, Pa), fusion temperature (T_m, K), Debye temperature (θ_D, K), linear thermal expansion ratio (α_T, K^{-1}), heat conductivity ratio (λ, W/см·K), thermal capacity ratio (C_p, J/mol·K) and also thermodynamic functions:

$\beta = (z \cdot E_a \cdot 1{,}602 \cdot 10^{-12}) / (27d^3)$;
$T_m = (E_a \cdot 1{,}602 \cdot 10^{-12}) / (41 \cdot k)$;
$\theta_D = 2{,}75 \cdot 10^6 \cdot (E_a / A)^{0,5} \cdot \hbar / (d \cdot k)$;
$\alpha_T = 3. k / (z \cdot E_a \cdot 1{,}602 \cdot 10^{-12})$;
$\lambda_F = z^{0,5} \cdot E_a \cdot k \cdot 4.10^{-21} / (d \cdot \hbar)$;
$C_p = (8.3 \cdot 10^{16} \cdot k \cdot T^2/\theta_D^2) \cdot (1.5\text{-}T/\theta_D)$ for $T<\theta_D$**;**.
$\Delta H_T = -E_a + \int C_p\, dT$; $\Delta S_T = \int (C_P/T)\, dT$;
$\Delta F_T = \Delta H_T - T \cdot \Delta S_T$.

Here: E_a, ΔH_T, ΔF_T (eV/atom), z is a coordination number of the nearest surroundings, d is an average distance between atoms in such surroundings (cm), $k = 1{,}38 \times 10^{-16}$ erg·K^{-1}, $\hbar = 1{,}05 \times 10^{-27}$ erg·s (the Boltsman's constant and Planck's one accordingly), A is a atomic weight in atomic units.

Table 1. Electronic spectrum and parameters of PrH_2, eV

Hydrides		**Initial state**	
Level Energy	**Popu - lation**	**Level Energy**	**Electron Population**
7÷11A1 0,6 ÷ 2			
$4A_2$, $6A_1$ – 4, –3	$5 \div 7B_2$ $-2 \div -1$		
$4B_2$ – 5,73		(Pr 6 s^2)×2 – 5.77	↓↑ ↓↑
$2B_1$ – 7,2			
$3A_2$ – 8,10			
$5A_1$ – 8,14			
$4A_1$ – 8,31		(Pr–5 d^2)×2 – 9.42	↓↑ ↓↑
$3B_2$ – 11,7			
$3A_1$ – 12,2			
$2A_1$ – 14,2		**(H– $1s^1$)×4** – 13.6	↓↑ ↓↑
$2A_2$ –14,15	↓↑		
$2B_2$ – 19,0	↓↑		
$1A_2$ – 19,2	↓↑		
$1B_2$ – 20,5	↓↑		
$1B_1$ – 22,5	↓↑		
$1A_1$ – 23,4	↓↑		

The calculated elastic - and thermodynamic parameters of bi- and tri- REM hydrides are given in table 2.

Table 2. Elastic and thermodynamics parameters of bi- and tri- REM hydrides

	YH_2	LaH_2	CeH_2	PrH_2	YH_3	LaH_3	CeH_3	PrH_3
A, atomic weight	30.3	46.97	47.37	47.63	22.98	35.48	35.78	35.98
Z, coordi-nation number	5.33	5.33	5.33	5.33	7.25	7.25	7.25	7.25
$\mathbf{E_{ат}}$, eV/atom	3.56	3.65	3.62	3.42	3.12	3.21	2.98	3.14
$\mathbf{\Delta F_{at}}$, eV/атом	3.55	3.64	3.61	3.40	3.11	3.20	2.97	3.13
d, 10^{-8} cm	2.09	2.15	2.11	2.10	2.09	2.15	2.11	2.10
β, 10^{10} Pa	15.9	14.9	15.7	15.0	18.9	17.9	17.5	18.8
T, melting point, K	1290	1320	1310	1240	1130	1160	1080	1140
$\mathbf{\Theta_D}$, K	437	345	349	340	469	373	364	375
TER, 10^{-6} 1/K	10.4	10.2	10.3	10.9	8.76	8.51	9.17	8.70
$\mathbf{C_p}$, 10^{-6} eV/ atom·K	6.22	9.47	9.30	9.74	5.45	8.28	8.62	8.20

In the data resulted in table 2 appreciable correlation between separate parameters is clear visible. The pair correlation ratios between atomic-electronic and elastic-thermodynamic parameters MH_X are resulted in table 3.

Table 3. Pair correlation ratios between two groups of parameters.

Para-meter		Elastic and thermodynamic parameters					
		ΔF_{at}	T_m	β	Θ_D	TER	C_p
Electronic-atomic	E_{at}	1.0	1.0	-0.9	-0.3	0.79	0.3
	A	0.6	0.6	-0.8	-1.0	0.66	0.96
	Z	0.93	-0.9	0.9	0.3	-0.9	-0.4
	X	-0.9	-0.9	0.9	0.4	-0.9	-0.4

From the resulted data the good dependences of energy of Gibbs and fusion temperature of synonymic type on the energy of atomization of investigated hydrides and of antibate type – on the hydrogen content in them are clear visible. The module of all-round compression is synonymously connected with content of hydrogen and number of coordination of the closest surroundings in hydrides, and the factor of thermal expansion is antibately connected with these parameters. The temperature of Debye and thermal capacity are unequivocally connected with average atomic weight of REM hydrides, only for the first parameter this communication is antibate, and for the second - is synonymic.

Conclusions

Correlation link is established in power and concentration aspects of electronic–atomic parameters with parameters of elastic– and thermodynamic condition of investigated REM hydrides. It is shown that power dependence is priority and concentration is less unequivocal. Obtained data can be used for optimization of hydrogenation and dehydrogenation processes of REM.

References

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