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A principal compound analysis and artificial neural network to predict the formation enthalpy for rare-earth dihydrides CeH$_2$

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Abstract——**In this paper, an attempt has been made to study and estimate the formation enthalpy for CeH$_2$ hydrides, by mean of a principal component analysis (PCA) is applied to select the significant modeling inputs and simplify the model structure. An artificial neural network (ANN) with 3-13-1 architercture structure has been developed to estimate ΔH. The structural parameter, elastic properties and formation enthalpy of Ce and CeH$_2$ were calculated by the density functional theory (DFT+U). The results of ΔH calculated with both ANN and DFT+U are basically consistent and are in good agreement with the experimental data. The adopted ANN structure provided an advantageous technique in predicting the non-linear relationship between the formation enthalpy and its influences factors (a, R, χ) which were previously selected by PCA.**

Keywords—**CeH$_2$ hydrides; Artificial neural network; Principal component analysis; First-principles calculations.**

I. INTRODUCTION

Rare-earth dihydride (CeH$_2$) have attracted particular attention [1,2]. Since, the above properties have great dependency on the structural parameters, therefore, it is important to understand the correlation between chemical and physical elements, as well as the thermodynamic properties. It is know that the enthalpy of formation plays a key role in energy balance calculation, combustion properties, equilibrium constants of reactions and fuel characteristics of materials [3,4]. Several methods have been carried out in calculating and estimating the formation enthalpy, such as semi-emperical band structure model [5], the Miedema model [6], group contribution approach [4,7,8] and density functional theory (DFT) calculations [9]. J.F. Herbst [10] has used the Miedema's model to estimate the formation enthalpy for binary AH$_x$ (x = 1-3) and ternary AB$_n$H$_x$ (n=1,2,3,5) hydrides, while Bououdina et al [11] extended a modified Miedema model to estimate the formation enthalpy of quaternary ZrCr$_{2(1-x)}$M$_{2x}$H$_2$ hydrides. For Al-Fe-Zr-Nd system, Lei Zhang et al. [12] have calculated the formation enthalpy by using a modified geometrical based model and Miedema's theory. A. Klaveness et al. [5] have used the semi-empirical method for According to the investigated methods, it is obvious that the theoretical models might provide good and accurate values for the formation enthalpy.

The principle component analysis (PCA) is used to select and identify the minimum of inputs variables necessary to capture all information of a system [13,14]. However, artificial neural network (ANN) is employed to predict and estimate variable related problems in complicated non-linear system [15-17] . This paper has three related objectives: (i) select the significant modelling inputs and simplify the model structure, by applying PCA; ii) predict the formation enthalpy from CeH$_2$ rare earth hydrides by using the ANN model; iii) and compare them with the results obtained by the density functional theory calculations (DFT+U).

This paper is organized as follows. In section 2, we briefly described the computational methods used in this study. In section 3, we presented the obtained results. Finally, a conclusion of the present work is given.

II. COMPUTATIONAL METHODS

II.1 *Datamining approach*

A.1.1 *Principal component analysis theory*

Principal component analysis (PCA) is one of the multivariate techniques to reduce the dimensionality of the dataset which involves many variables [18,19]. The original matrix data is decomposed and project into two plots, the sample are classified in the score plot and the descriptors in terms of their separation of the samples in loading plot following the principal component (PCs) axis [13,20].

B.1.2 *Artificial neural network theory*

An artificial neural network (ANN) is a biologically inspired processing unit that is extensively used to identify and to model non-linear systems [15]. A typical ANN architecture is composed of the interconnected layers, an input layer, one or more hidden layer and an output layer, each of which was formed by a determined number of neurons.

The relationship between the inputs and the output can be written as [16,17]:

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$$y = f(\sum_{i=1}^{n} w_i x_i + \theta) \qquad (1)$$

where x_i and y are the i inputs and output respectively, w_i the weight of the neural model, θ is the bias and f is the activation function.

The mean square error (MSE) and coefficient of determination R^2, were used to evaluate the performance of training process, the computational equations of these error indexes are given by:

$$MSE = \frac{1}{N} \sum_{i=1}^{N} (t_i - o_i)^2 \qquad (2)$$

$$R^2 = 1 - \left(\frac{\sum_{i=1}^{N} (t_i - o_i)^2}{\sum_{i=1}^{N} (o_i)^2} \right) \qquad (3)$$

where N is the number of training patterns, t_i is the desired output and o_i is the calculated network output.

In this work a multilayer perceptron MLP [21] has used to estimate the formation enthalpy. More details about the calculation using MLP, can be found in our previous work [17].

C.1.3 Density functional theory

The first-principles calculations were performed with the full-potential linear augmented plane wave (FP-LAPW) method [22] within the density functional theory (DFT) improved by an on-site Coulomb self-interaction potential (DFT+U) [23-26] as implemented in the WIEN2k code [27]. The exchange-correlation potential for structural properties was calculated by the generalized gradient approximation correction GGA+U [26-28], in which a Hubbard U term corresponding to the mean-field approximation of the on-site Coulomb interaction is added to the (GGA-PBE) functional [29], for describing the "strongly correlated" electronic states of the Ce 4f-states in dihydride, as well as for systems with localized d-electrons and f-electrons [30,31]. The Hubbard-type on-site Coulomb interaction has been considered by employing a rotationally invariant method proposed by S.L. Dudarev et al. [26]. In our calculations, we apply the Hubbard parameter U correction on Ce 4f electrons and it was chosen to be 4.0 eV for Ce and CeH_2. The total energy was minimized by using the value of 7 Ryd for the cut-off energy and 18 for G_{max} was used in a Fourier expansion of potential in the interstitial region. The Brillouin zone integration is performed using a k-mesh of $11 \times 11 \times 11$ meshes for Ce and CeH_2 calculations.

The formation enthalpy of CeH_2 is calculated according:

Ce + H$_2$ → CeH$_2$
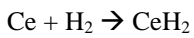
$$\Delta H (CeH_2) = Etot (CeH_2) - Etot (Ce) - Etot (H_2) \qquad (4)$$

where Etot(CeH_2), Etot(Ce) and Etot(H$_2$) are the total energy of the hydrides compounds, pure element Ce and gaseous H$_2$ molecule, respectively.

III. RESULTS AND DISCUSSION

In order to select and identify the minimum of inputs variables by the PCA, a database for several hydrides was collected from literatures [10,32-34], include the lattice parameter (a), elastic constants (C_{ij}), bulk modulus (B), shear modulus (G), formation enthalpy (ΔH) for different hydrides, and Pauling electronegativity (χ), atomic radius (R) for rare earth element forming these hydrides. From PCA analysis, the first axis PC1 captures 60.305 % of the variance in the datasets, whereas PC2 captures only 33.016 %. These results are shown in Fig. 1a and b.

The PC2 capture the variation in both the formation enthalpy (ΔH) and the bulk modulus (B). We can notice that hydrides namely [LaH$_2$, YH$_2$, ScH$_2$] (cluster 1) with low bulk modulus, have low formation enthalpy, respectively and have a positive PC2. While hydrides namely [NbH$_2$, VH$_2$, CrH$_2$] (cluster 2) with high bulk modulus have high formation enthalpy, and have a negative PC2. In addition, negative PC2 values related with low a, low R and high χ, positive PC2 values representing high a, high R and low χ.
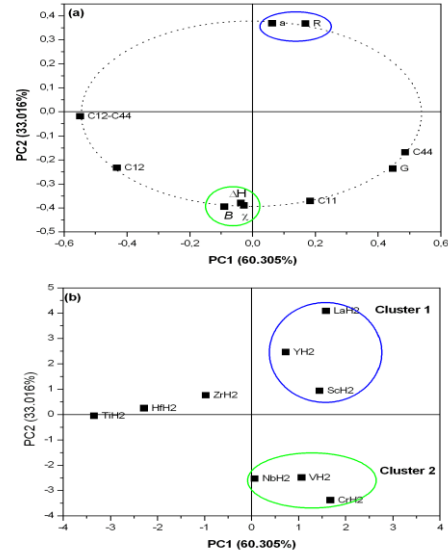

Fig. 1. Results of PCA analysis on data, (a) PCA loadings plot, (b) PCA scores plot.

A high correlation between (ΔH) and (B), (a), (R) and (χ) has been observed in the previous PCA analysis. Hence, the a, R and χ might be used as inputs of the selected ANN, while formation enthalpy ΔH as output.

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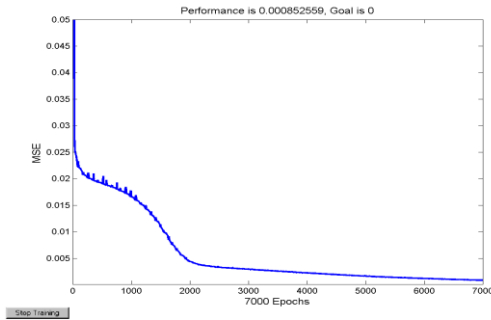Ghardaïa – Algeria 24 - 25 Octobre 2016

Fig. 2. Training artificial neural network (3-13-1) model for formation enthalpy

All inputs and outputs in the data sets are normalized to the interval [-0.5,+0.5] according to:

$$x_{normalized} = \frac{(x - x_{min})}{(x_{max} - x_{min})} - 0.5 \qquad (5)$$

After training and testing processes, the performance of the ANN is analyzed. During the training model, the average mean square error (MSE) decreased with increasing the number of iteration. The curve illustrated in Figure 2 indicates that the convergence with MSE equal to 8.525×10^{-4} is achieved after 7000 training iterations.

The predicted values of formation enthalpy (ΔH) for CeH$_2$ hydrides by the ANN (3-13-1) model is -202 kJ/mol H$_2$. Compared with the experimental values [35], the relative errors are 1.94 % for CeH$_2$ hydrides. Therefore, the formation enthalpy predicted by an ANN model is in good agreement with the experimental values.
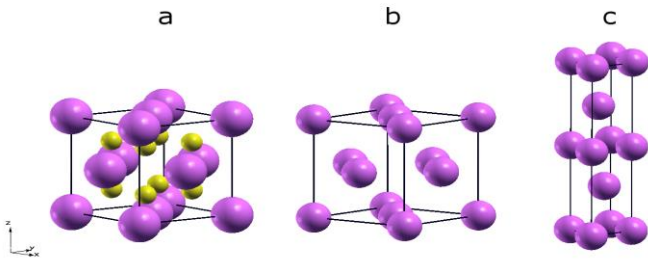

Fig. 3. Units cells of (a) the fluorite-type structure Fm-3m (225) of CeH2, (b) the cubic Fm-3m (225) of Ce.

The rare earth element Ce and its dihydride CeH$_2$ have a cubic structure and fluorite-type structure (CaF$_2$), respectively [36]; designated by the space group *Fm-3m* (225), as shown in Fig. 3a and 3b, in which Ce and H atoms occupy Wyckoff position 4a (0, 0, 0) and 8c (1/4, 1/4, 1/4). The equilibrium lattice constant (a_0, c_0), energy (E_0), bulk modulus (B) and pressure derivative (B') of the studied rare earth element and their

hydrides have been computed at the ground state using Birch-Murnaghan equation of state (EOS) [37]. The bulk modulus (B) for Ce and CeH$_2$ compounds is found to be 23.17 and 58.01 GPa, respectively. The obtained results as well as the corresponding experimental and theoretical values are reported in Table 1. From this Table, we note that our calculated structural parameters (a_0, c_0), bulk modulus (B), pressure derivative (B') for hydrides and rare earth elements are in good agreement with the reported experimental and theoretical values [36,38]. The calculated bulk modulus is slightly lowered between rare-earth elements and their corresponding dihydrides in the sequence Ce < CeH$_2$ showing the effect of hydrogen (H$_2$) insertion within the crystal lattice of Ce element [39].

TABLE I:
Calculated lattice parameters (a0, c0), bulk modulus (B), pressure derivative (B') for Ce and CeH$_2$ hydrides.

system	Phase		U(eV)	a_0 (Å)	B (GPa)	B'
Ce	Fcc	GGA+U	4	5.18	23.17	4.27
		Exp.		5.14[a]	22[a]	
		Other		5.011[b]	19[b]	
CeH2	CaF$_2$	GGA+U	4	5.58	58.01	4.66
		Exp.		5.61[a]		
		Other		5.562[b]	60[b]	

[a] Ref.[36], [b] Ref.[38]

From Eq. (4) and at equilibrium energies which are obtained by Birch-Murnaghan equation of state (EOS), the enthalpy of formation for CeH$_2$ were calculated, and are -195 kJ/mol H$_2$, and is reported in Table 2, which are in excellent agreement with available experimental data [35]. Suggesting that the cubic structure of CeH$_2$ is stable and the reaction is an exothermic reaction.

TABLE II: Calculated formation enthalpy (ΔH) for CeH$_2$ by the DFT+U and the ANN.

CeH$_2$	Methods		
	ANN	DFT+U	EXP
ΔH (kJ/mol H$_2$)	-202	-195	-206[a]

[a] Ref.[35].

The comparison between different prediction models (ANN and DFT+U) and experimental data are listed in the Table 2. The relative error between the two independent methods is about 3.59 % for CeH$_2$. It is seen that the formation enthalpies obtained by the ANN model are basically consistent with the obtained one by the quantum calculations (DFT+U) and are in good agreement with the experimental data. Indicating that the constructed ANN model is capable to predict accurately the formation enthalpy as a function of the lattice parameter (a), atomic radius (R) and the Pauling electronegativity (χ).

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IV. CONCLUSIONS

In this paper, a three input variables are selected by the principal component analysis (PCA), such a lattice parameter (a) of hydrides, atomic radius (R) and Pauling electronegativity (χ) of rare-earth element forming these hydrides. The ANN with 3-13-1 architecture was selected to estimate the formation enthalpy. The obtained result is about -202 kJ/molH$_2$. From the DFT+U calculations, the structural parameters and the elastic properties for Ce and CeH$_2$ are investigated. The calculated lattice parameters, bulk modulus, and pressure derivative show quite consistency with other available experimental and theoretical results. Also, the formation enthalpy for CeH$_2$ hydrides is determined. The obtained value ΔH is found to be -195 kJ/mol H$_2$, suggesting that the reaction for CeH$_2$ is an exothermic reaction. These results are in good agreement with the experimental data. The relative error of ΔH obtained between ANN model and DFT +U calculations is about 3.59 %. It is seen that the formation enthalpy obtained by the ANN model are basically consistent with obtained by the quantum calculations (DFT+U) and are in good agreement with the experimental data.

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