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Correlation of Structural properties with Thermodynamic Properties for Multi-Element AB_5-Type Hydrogen Storage Alloy

Niyanta Garkoti[1], Kuldeep Panwar[2] and Sumita Srivastava[2]

[1] M.Sc. III Semester, Department of Physics, Pt. L.M.S. Government Post Graduate College, Rishikesh (Autonomous College) Dehradun-249201, India

[2] Department of Physics, Pt. L.M.S. Government Post Graduate College, Rishikesh (Autonomous College) Dehradun-249201, India

niyanta.garkoti@gmail.com

Abstract: Wide applications of hydrogen storage alloys have resulted in synthesis of multi-element alloys. Modifying the parent alloy by substitution gives alloys whose properties can differ from the parent alloy. Important thermodynamic properties of hydrogen storage alloys are heat of formation of hydride and plateau pressure. These properties are measured through experiment. In the present study, structural properties of a class of hydrogen storage alloys have been correlated with these thermodynamic properties. Based on this correlation one can predict of heat of formation of hydride and plateau pressure for alloys without actually synthesizing them.

Keywords: *AB_5-Type Hydrogen Storage Alloy, Heat of Formation, Plateu Pressure*

1. INTRODUCTION

Hydrogen storage alloys are materials, which absorb hydrogen at certain pressure and desorb it at a lower pressure. Hydrogen atom is stored in the solid material at interstitial position. State of the art hydrogen storage alloys are AB_5, AB_2, A_2B and AB type. Among so many hydrides, AB_5 is popular for its easy activation and operation at room temperature and at little atmospheric pressure [1-3]. Nowadays, most of the AB_5-type alloys are synthesized through substitution of other elements in the parent alloy either at 'A' or at 'B'sites. The specific requirements of hydrogenation properties are met through synthesizing actual alloy with trial and error method. In earlier studies, theoretical approach for explaining thermodynamic properties have been presented [4-7]. Such studies were mostly based on ternary hydrides. At present no such model is available, which can predict the multi-element alloy properties without actually synthesizing it. In the present investigation, structural properties like lattice parameter 'a', 'c', unit cell volume and a new parameter r_B* have been correlated with the observed thermodynamic properties like heat of formation of hydride and hydrogen plateau pressure. Whereas 'a', 'c' and unit cell volume are properties of the synthesized alloy, r_B* is an equivalent radius of B in AB_5 alloy after substitution at the 'B' site. A relation has been established between structural and thermodynamic properties, which can be used to predict thermodynamic parameters of alloys.

2. METHODOLOGY

In present investigation, three series of alloys have been studied. These alloy series are termed as alloy1, alloy2 and alloy3. The nomenclature of alloys is given in Table 1. For each alloy series, experimentally observed values of lattice parameters 'a' and 'c' along with heat of formation and hydrogen plateau pressure reported in literature have been noted. r_B* has been calculated by taking stoichiometric composition of various elements at 'B' and atomic radius of each element. The values of atomic radii for elements under present study are given in Table 2. Graphs have been plotted among structural and thermodynamic parameters for each alloy and a relation has been established.

Table 1- Nomenclature of alloys

S.N.	**Name of alloy**	**Composition of alloy**
1	Alloy 1	$LaNi_4R$ (R= Al, Mn, Fe, Cu, Co, Cr)
2	Alloy 2	$LaNi_{5-x-y-z}Al_xSn_yFe_z$
3	Alloy 3	$La_{0.78}Ce_{0.22}Ni_{3.73}Co_{0.30}Al_{0.1}7Fe_{0.5-x}Si_x$ (x = 0, 0.05, 0.075, 0.1)

Table 2- Atomic radius of elements using VWR Sargent Welch Periodic Table

S.N.	Element	Atomic Radius **(Å)**
1	La	2.74
2	Ce	2.70
3	Ni	1.62
4	Co	1.67
5	Mn	1.79
6	Fe	1.72
7	Si	1.46
8	Al	1.82
9	Cu	1.57
10	Cr	1.85

The equation for calculating r_B* used in the present investigation is given as Eq. 1. The calculation for one of the members of alloy 1 is also shown as an example.

$$r_B^* = (4\, r_{Ni} + r_{Al})/5 \qquad (1)$$

For example we consider the alloy $LaNi_4Al$, obtained by starting $LaNi_5$ and five Ni atoms in substituting one of the 5 Ni atoms by an Al atom. For this alloy $r_B^* = \{(4 \diamond 1.62) + 1.82\}/5 = 1.66$.

3. RESULTS AND DISCUSSIONS

Table 3 shows all the known and calculated parameters of alloy 1-$LaNi_4R$ hydride.

Table 3- Known and calculated parameters of alloy 1 $LaNi_4R$ hydride [7-10]

S.N.	Alloy	a (Å)	c (Å)	Unit cell Volume ($Å^3$)	r_B^*(Å)	Heat of formation (kcal/mol H)	Plateau pressure (atm)
1	$LaNi_5$	5.017	3.986	86.28	1.62	-6.33	3.0
2	$LaNi_4Co$	5.018	3.981	86.2	1.63	-7.43	1.2
3	$LaNi_4Cu$	5.033	4.007	87.29	1.61	-8.068	1.6
4	$LaNi_4Fe$	5.049	4.015	88.02	1.64	-8.87	1.05
5	$LaNi_4Cr$	5.07	4.048	90.23	1.666	-10.0	0.91
6	$LaNi_4Mn$	5.089	4.082	90.91	1.654	-11.6	0.05
7	$LaNi_4Al$	5.061	4.07	89.65	1.66	-13.1	0.01

Table 3 shows that, in most of the cases heat of formation and plateau pressure decrease with increasing value of the lattice parameters, unit cell volume and r_B^*. More negative is the value of the heat of formation, more stable is the corresponding hydride. Plateau pressure is related to the heat of formation. More negative is the value of heat of formation, smaller is the plateau pressure. The variation of heat of formation and plateau pressure with unit cell volume and r_B^* are shown in Figures 1, 2, 3 and 4 respectively.

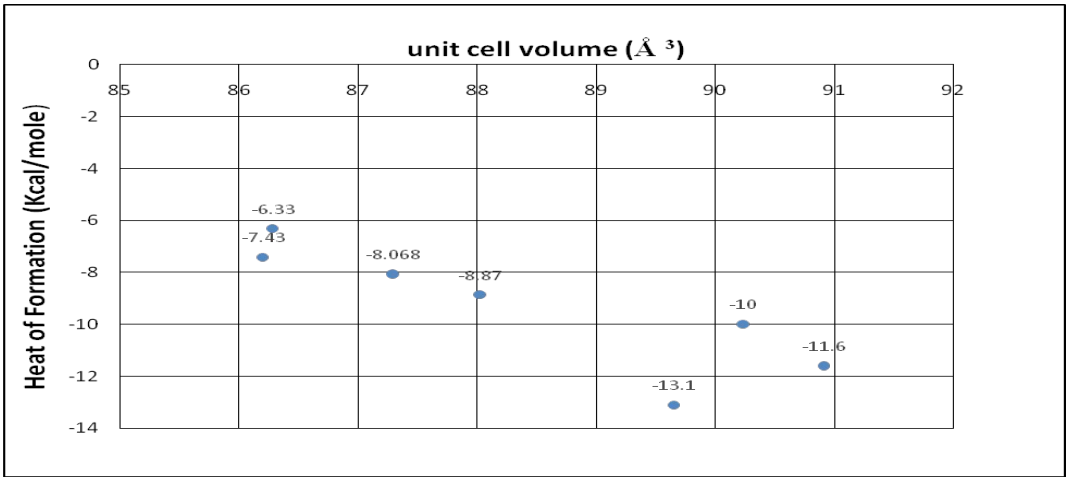

Figure 1- Variation of heat of formation with unit cell volume.

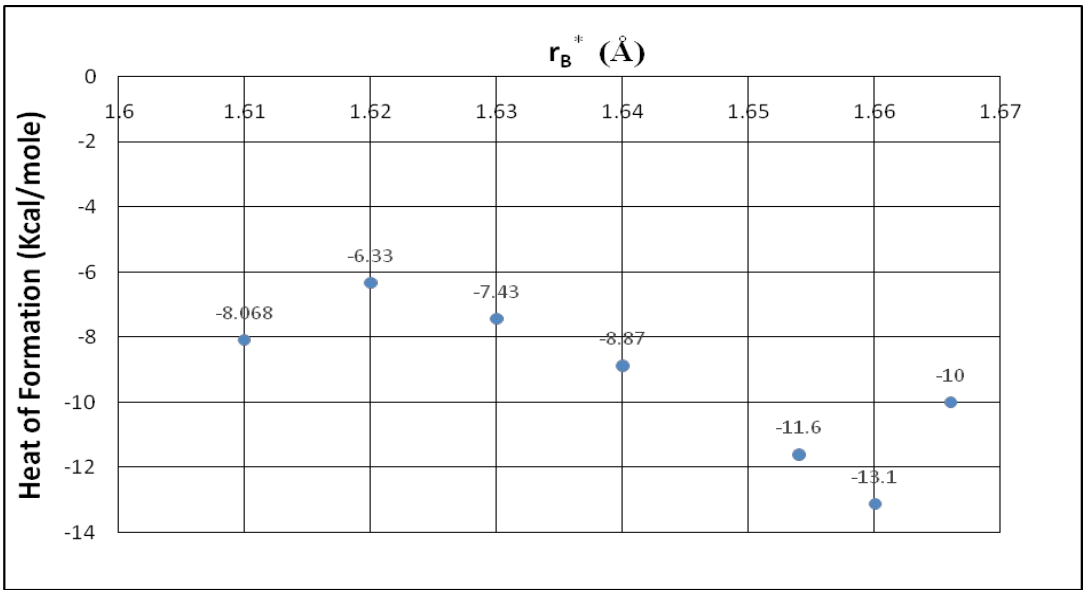

Figure 2- Variation of heat of formation with r_B^*.

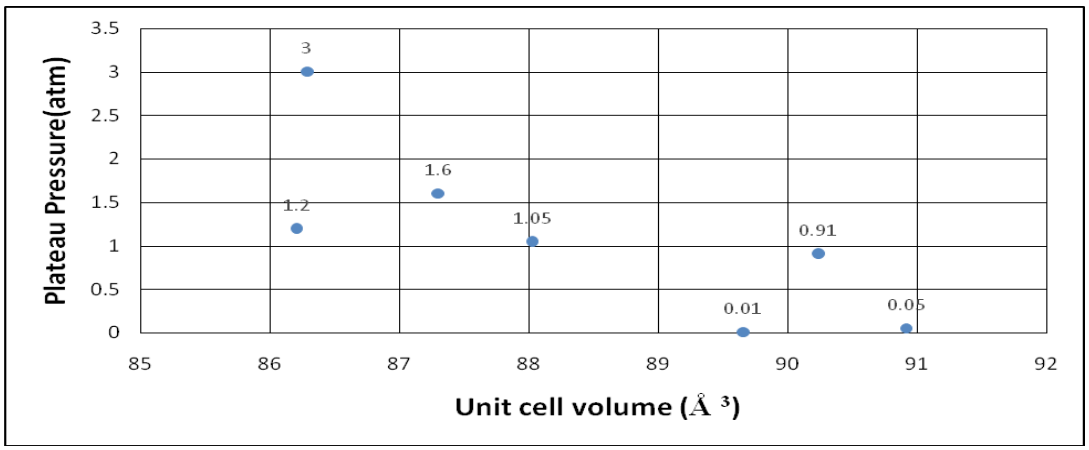

Figure 3- Variation of hydrogen plateau pressure with unit cell volume.

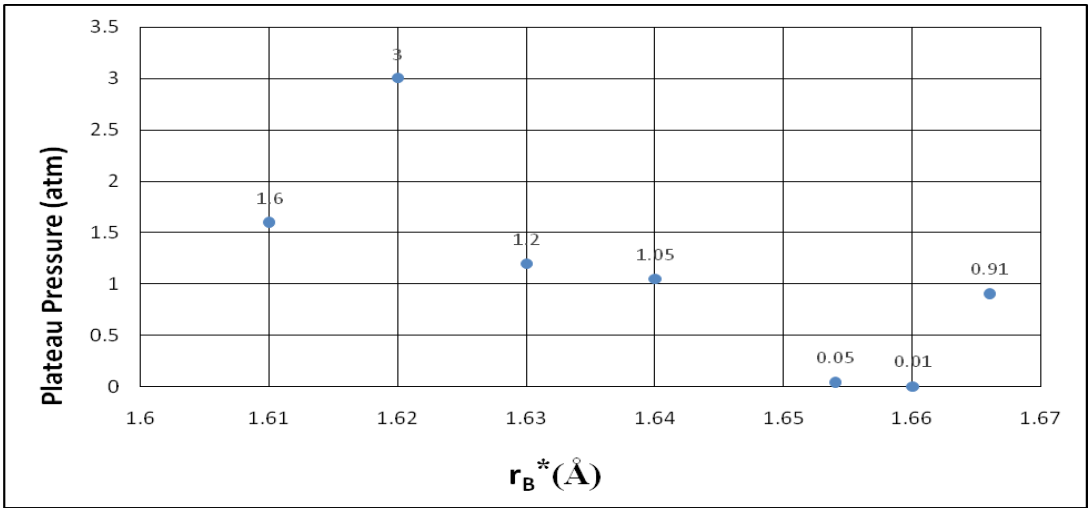

Figure 4- Variation of hydrogen plateau pressure with r_B^*.

The trend in heat of formation and plateau pressure are similar with unit cell volume and r_B^*. It may be mentioned here that unit cell volume is an experimental value obtained after the synthesis of the alloy and doing diffraction measurement, whereas r_B^* is a theoretically calculated value found without actually synthesizing the alloy. In this way, r_B^* can play a role similar to the unit cell volume. Hence by estimating the value of r_B^*, one can predict the trend of heat of formation and plateau pressure without synthesizing the actual alloy.

Similar known and calculated parameters of Alloy 2:$LaNi_{5-x-y-z}Al_xSn_yFe_z$ hydride are given in Table 4. This table also shows similar variation in heat of formation and hydrogen plateau pressure with unit cell volume and r_B^*. Both thermodynamic parameters decrease with structural parameters.

Table 4- known and calculated parameters of Alloy 2:$LaNi_{5-x-y-z}Al_xSn_yFe_z$ hydride [11]

S.N.	Alloy	a (Å)	c (Å)	Unit cell Volume ($Å^3$)	r_B^* (Å)	heat of formation kcal/mole H	Plateau Pressure (atm)
1	$LaNi_5$	5.1037	3.8936	84.1717	1.62	-6.33	0.500
2	$LaNi_{4.8}Sn_{0.1}Al_{0.1}$	5.0295	3.9987	86.9895	1.623	-8.56	0.071
3	$LaNi_{4.6}Fe_{0.2}Al_{0.2}$	5.0307	3.9997	87.0527	1.632	-8.8	0.049
4	$LaNi_{4.8}Sn_{0.2}$	5.0332	4.0107	87.3789	1.621	-8.18	0.063
5	$LaNi_{4.6}Sn_{0.2}Fe_{0.2}$	5.0403	4.0052	87.5055	1.628	-8.82	0.055

Table 5 shows same data for alloy3: $La_{0.78}Ce_{0.22}Ni_{3.73}Co_{0.30}Mn_{0.30}Al_{0.17}Fe_{0.5-x}Si_x$ multi-element hydride. In this case again, heat of formation and plateau pressure decrease with increasing value of unit cell volume. However, r_B^* does not show clear tendency of increase or decrease of heat of formation and plateau pressure. It may be due to substitution also at 'A' site.

Table 5- known and calculated parameters of Alloy 3: $La_{0.78}Ce_{0.22}Ni_{3.73}Co_{0.30}Mn_{0.30}Al_{0.17}Fe_{0.5-x}Si_x$ multi-element hydride [12]

S.N.	Alloy with x	a (Å)	c (Å)	unit cell volume ($Å^3$)	r_B^* (Å)	Heat of Formation (kcal/mole H)	Plateau pressure (atm)
1	0	5.03	4.045	88.0142	1.65	-6.584	0.5
2	0.05	5.03	4.046	88.0359	1.647	-7.514	0.45
3	0.075	5.031	4.05	88.158	1.646	-8.808	0.2
4	0.1	5.035	4.048	88.2547	1.639	-8.65	0.1

As pointed out earlier in this paper, heat of formation of hydride is a measure of the stability of the hydride. More negative is the value of the heat of formation, more stabile is the corresponding hydride. Due to stability of the hydride, hydrogen absorption may take place at lower hydrogen pressures. Further, it may be mentioned here that increased value of the unit cell volume facilitates the hydrogen absorption at a lower driving force, resulting in lower plateau pressure. These two factors are plausible explanation of the correlations observed between heat of formation of hydrides, stability of hydride, hydrogen plateau pressure and unit cell volume.

4. CONCLUSIONS

From above discussion, we conclude that the heat of formation and plateau pressure decreases with increasing value of unit cell volume in all the three class of alloys under study. Similar trends of heat of formation and plateau pressure are observed with r_B^* also. Since unit cell volume is an experimental value, structural parameter r_B^* can be used instead for predicting heat of formation and plateau pressure for an alloy without actually synthesizing it.

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