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Roles of the hydride forming and non-forming elements in hydrogen storage alloys

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Abstract

The electronic structures of small octahedral model clusters containing hydrogen, 3d, 4d, 5d transition and non-transition elements are investigated by the DV-Xα molecular orbital method. It is found that hydrogen makes a strong chemical bond with the hydride non-forming elements, B, as long as the hydride forming elements, A, exist in the neighborhood. This is a reason why hydrogen is located preferentially near the hydride non-forming elements in many hydrides. Also it is suggested that the ratio of the A–B bond strength to the A–A bond strength lies in a certain range for conventional hydrogen storage A–B alloys.

Keywords: Electronic structure; Hydride; Hydrogen storage alloy; Molecular orbital method

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1. Introduction

Hydrogen storage alloys such as $LaNi_5$ (AB_5-type), $ZrMn_2$ (AB_2-type), TiFe (AB-type) and Mg_2Ni (A_2B-type) consist of hydride forming element (A) and non-forming element (B). We may speculate about the role of each element in the following way. The hydride forming element (e.g., La) may make a strong chemical bond with hydrogen and easily forms a stable hydride (e.g. LaH_2). On the other hand, the hydride non-forming element (e.g. Ni) may work to reduce such a strong A–H bond, so that it could activate the hydrogen desorption process.

However this naive understanding is not true, because hydrogen is located closer to B elements in the hydride, and makes a stronger chemical bond with B elements than A elements [1–5]. For example, the electronic structures of $LaNi_5H_6$ hydride are calculated using a cluster model shown in Fig. 1(a), and a contour map of the electron density distribution is shown in Fig. 1(b) on the lattice plane where all the La, Ni and H atoms lie. As shown in this figure, the relatively high electron-density region near hydrogen extends towards the Ni atom site, but does not towards the La atom site. This result clearly indicates that hydrogen has a larger affinity for Ni atoms than La atoms in $LaNi_5H_6$. This trend has also been observed in other hydrogen storage alloys such as $ZrMn_2$ and Mg_2Ni. Thus, the presence of strong B–H interactions is a general trend characteristic and is a feature of hydrogen storage alloys. However, hydride forming elements may also play an important role because if there is no A element in the alloy, hydrogen is never absorbed in it.

Therefore, it is important to understand further the roles of hydride forming and non-forming elements in order to design and develop new types of hydrogen storage alloys. For this purpose, a series of calculations of the electronic structures is performed using small model clusters. The DV-Xα cluster method is employed in this study.

2. DV-Xα cluster method and cluster model

The DV-Xα cluster method is a molecular orbital calculating method based on the Hartree-Fock Slater approximation. The detailed explanation of this method is given elsewhere [6,7].

According to our previous study [8], a local electronic structure in a small metal polyhedron containing hydrogen is important in understanding qualitative features of hydrogen storage alloys. So, as shown in Fig. 2, an octahedral cluster model, M_2X_4, and its hydrogenated cluster model, HM_2X_4, are employed in the present calculation, where X is set to be the either Ni or Ti. Hydrogen is placed at the center of the octahedron. Here, Ni is a hydride non-forming element, but Ti is a hydride forming element. A

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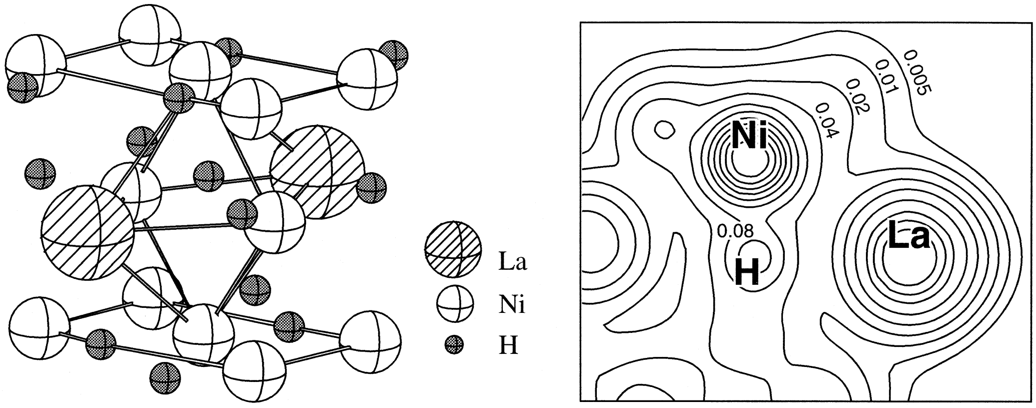

(a) (b)

Fig. 1. (a) Cluster model used in the calculation and (b) contour map of the electron density distribution for $LaNi_5H_6$. The denoted numbers indicate the numbers of electron per a.u.^{3} (1 a.u.=0.0529 nm).

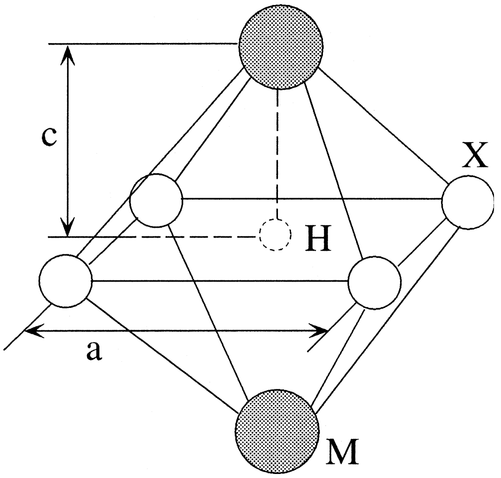

Fig. 2. Octahedral cluster model used in the calculation.

variety of transition elements and non-transition elements are selected for M. In these cluster models, the *a*-axial length is fixed at a value twice as large as the atomic radius of Ni or Ti, and the *c*-axial length is varied following the atomic radius of M so that the M atom sphere contacts with the X atom sphere as if they are rigid-body spheres. Therefore, the atomic sizes of M are taken into account in these cluster models.

3. Results and discussion

3.1. Bond order between atoms in Ni and Ti containing clusters

The bond order is the overlap population of the electrons between atoms. This is a measure of the strength of the

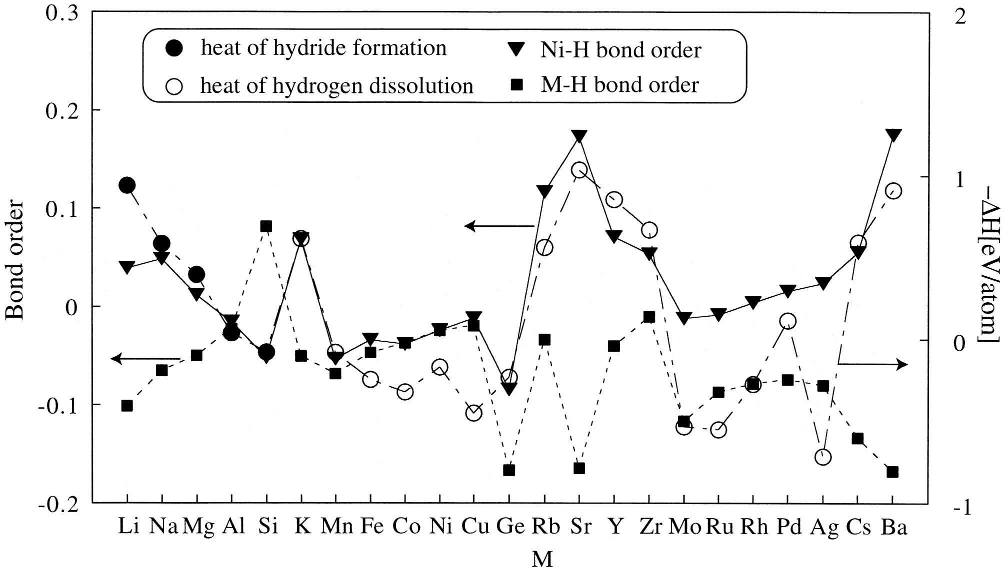

Fig. 3. Bond orders between Ni and H atoms and between M and H atoms in HM_2Ni_4 cluster, and comparison with heat of hydride formation of M metal or heat of hydrogen dissolution in M metal.

covalent bond between atoms. Fig. 3 shows the bond orders between metal and hydrogen atoms in the Ni-containing octahedral cluster, HM_2Ni_4. Every bond order shown in this figure is the value per atomic bond in the cluster. As is evident from Fig. 3, the Ni–M bond order is large when the M–H bond order is small. In particular, the Ni–H bond order is enhanced when the M's are the hydride forming elements such as Na, Sr, and Ba. This means that hydrogen interacts strongly with Ni atoms if the hydride forming elements exist in the neighborhood, in agreement with the result shown in Fig. 1 or some previous calculations of electronic structures of Ni-containing hydrides [1,2]. On the other hand, when the M's are the hydride non-forming elements such as Fe, Co, and Ni, the Ni–H bond order is very small and hence there is no chance for hydrogen to absorb in such a B-alone cluster or alloy. Thus, the Ni–H bond order correlates well with the heat of hydride formation of M metal or the heat of hydrogen dissolution in M metal, ΔH, as shown by a dotted line in Fig. 3.

As shown in Fig. 4, a similar trend is seen in the Ti-containing octahedral cluster, HM_2Ti_4. As mentioned before, in contrast to Ni, Ti is a hydride forming element. When the M's are hydride non-forming elements (e.g., Fe, Co and Ni), the Ti–H bond orders are smaller than the M–H bond order. When the M's are stronger hydride forming elements than Ti, for example Sr, Y and Ba, the Ti–H bond order is larger than the M–H bond order. As a result, the Ti–H bond order curve resembles the $-\Delta H$ curve as shown in Fig. 4.

A similar result is also obtained in the Mg-containing octahedral cluster, HM_2Mg_4. Therefore, the present result is supposed to be one of important features of hydrogen storage alloys.

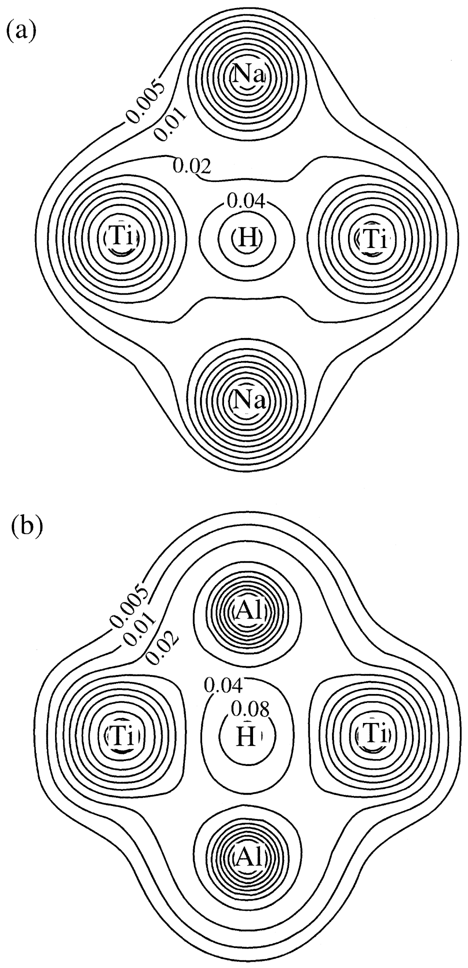

Fig. 5. Spatial electron density distribution on the (110) atomic plane for (a) HNa_2Ti_4 and (b) HAl_2Ti_4. The denoted numbers indicate the numbers of electron per a.u.^{3} (1 a.u.=0.0529 nm).

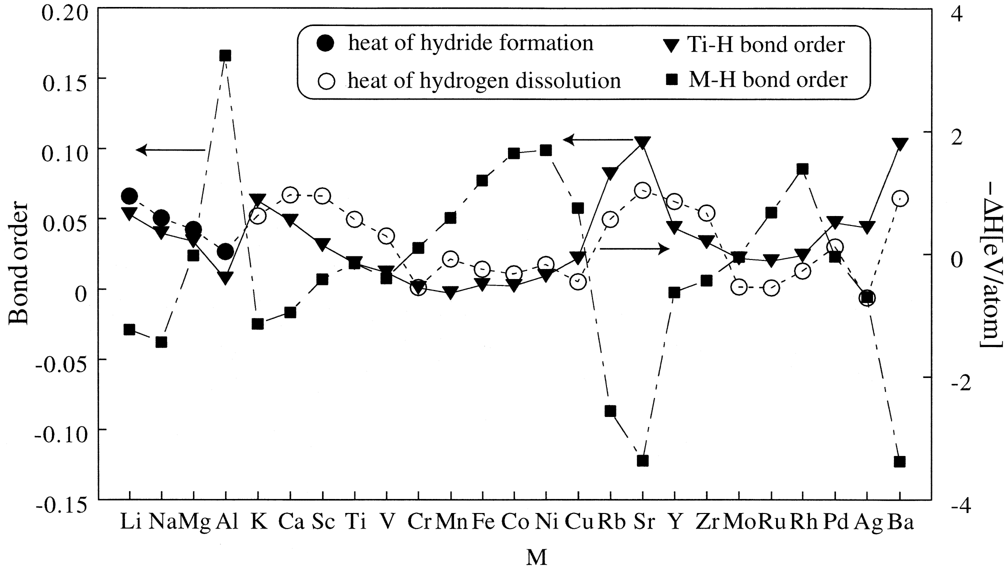

Fig. 4. Bond orders Ti and H atoms and between M and H atoms in HM_2Ti_4 cluster, and comparison with heat of hydride formation of M metal or heat of hydrogen dissolution in M metal.

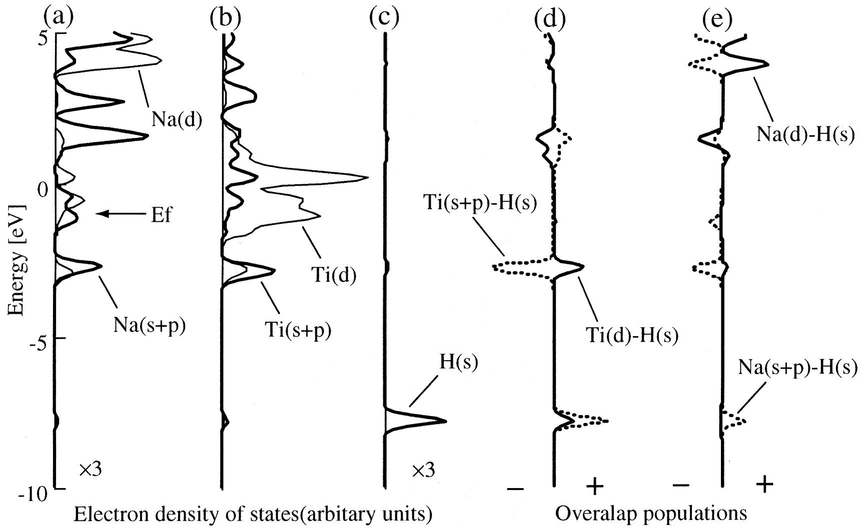

Fig. 6. Partial density of states and energy distribution of overlap populations for HNa_2Ti_4 cluster.

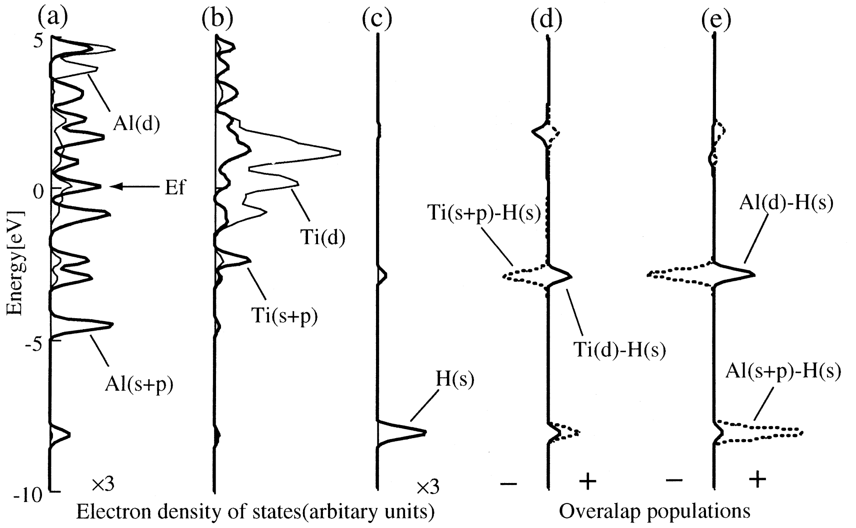

Fig. 7. Partial density of states and energy distribution of overlap populations for HAl_2Ti_4 cluster.

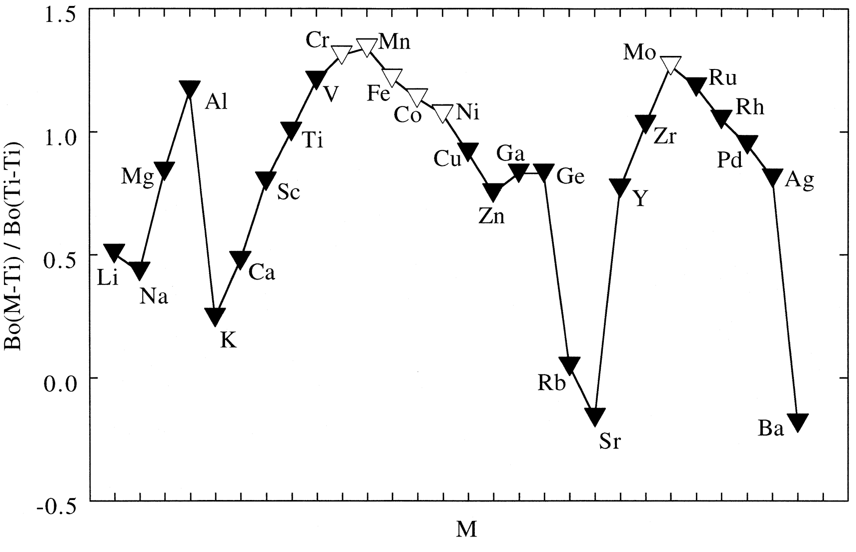

Fig. 8. Change in the bond order ratio with M in M_2Ti_4 cluster.

3.2. Spatial electron density distribution

The spatial electron density distribution is shown in Fig. 5(a) for HNa_2Ti_4 cluster and (b) for HAl_2Ti_4 cluster. From the result of the HNa_2Ti_4 cluster shown in Fig. 5(a), it is apparent that hydrogen interacts more strongly with Ti atoms than Na atoms, despite hydrogen having a larger affinity for Na atoms than Ti atoms in the binary metal–hydrogen system. On the other hand, in case of the HAl_2Ti_4 cluster, the electron density distribution around H is extended towards the Al atoms, but not towards the Ti atoms. This implies that hydrogen interacts more strongly with Al atom than Ti atoms, in agreement with the result of bond order calculations shown in Fig. 4.

3.3. Partial electron density of states and energy distribution of overlap populations

In order to explain these bond order changes with M, partial density of states and energy distribution of overlap populations are calculated for two clusters, HNa_2Ti_4 and HAl_2Ti_4 and the results are shown in Figs. 6 and 7, respectively. In each figure, (a), (b) and (c) show the results of the partial density of states and (d), (e) show the results of the energy distribution of the overlap populations. The Fermi energy level, E_f, is indicated by an arrow in (a) in each figure.

The partial densities of states for Na components shown in Fig. 6(a) are extended mainly over the higher energy region than the E_f, whereas the partial densities of states for Al components shown in Fig. 7(a) are distributed over the energy region well below the E_f. In fact, the Al(s+p) and Al(d) components appear even in the hydrogen related orbital levels near -8 eV and -3 eV. As a result, as shown in Fig. 7(e), the Al(s+p)–H(s) and the Al(d)–H(s) overlap populations become larger, as compared to the Na(s+p)–H(s) and the Na(d)–H(s) overlap populations shown in Fig. 6(e). In particular, the Al(d)–H(s) overlap populations are both positive at -8 eV and -3 eV, indicating that the bonding-type interaction is operating between them. In contrast to this, the Na(d)–H(s) overlap population is nearly nil. This difference will cause the Al–H bond order to be larger than the Na–H bond order as shown in Fig. 4.

On the other hand, as shown in Fig. 6(d) and Fig. 7(d), the Ti(d)–H(s) or the Ti(s+p)–H(s) overlap population is larger in the HNa_2Ti_4 cluster than in the HAl_2Ti_4 cluster. This probably causes the slightly larger Ti–H bond order in the HNa_2Ti_4 cluster than in the HAl_2Ti_4 cluster, as shown in Fig. 4.

3.4. Metal–metal interaction in hydrogen storage alloys

For $LaNi_5$, TiFe and $ZrMn_2$, hydrogen atoms occupy a part of the interstitial sites in the crystal lattice of the alloy. Any substantial changes of the crystal structure do not occur during hydrogenation except for the onset of lattice expansion and distortion in them. In this case it is supposed that the easiness of the lattice expansion and distortion during hydrogenation may be controlled by the strength of chemical bonds between metal atoms in the starting alloy [8]. In fact the hydride stability correlates well with the ratio of bond orders between constituent metal atoms in these alloys [1,8–10].

On the analogy of this approach, the bond order ratio is defined as Bo(M–Ti)/Bo(Ti–Ti). Here, Bo(M–Ti) and Bo(Ti–Ti) are the M–Ti and Ti–Ti bond order, respectively. From the calculation of the M_2Ti_4 cluster, this ratio is estimated and the result is shown in Fig. 8. The hydrogen storage alloys are denoted by open triangles in this figure. For example, M=Fe means TiFe.

It is known that the hydride stability changes in the order, TiNi>TiCo>TiFe. This is the same order as the calculated bond order ratios. The hydride becomes more unstable with increasing bond order ratio. This result is also consistent with our previous result of alloyed TiFe [10]. It is interesting to note here that all the hydrogen storage alloys have the bond order ratio larger than unity as shown as Fig. 8.

4. Conclusion

There is a general trend that hydrogen makes a stronger chemical bond with hydride non-forming elements as long as hydride forming elements exist near them in hydrogen storage alloys containing Ni or Ti.

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