Journal of Alloys and Compounds 253–254 (1997) 322–325

Alloying effect on the electronic structures of hydrogen storage compounds

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Abstract

The electronic structures of hydrogenated $LaNi_5$ containing various 3d transition elements were investigated by the DV-Xα molecular orbital method. The hydrogen atom was found to form a strong chemical bond with the Ni rather than the La atoms. The alloying modified the chemical bond strengths between atoms in a small metal octahedron containing a hydrogen atom at the center, resulting in the change in the hydrogen absorption and desorption characteristics of $LaNi_5$ with alloying.

Keywords: Electronic structure; Hydride; $LaNi_5$; Mg_2Ni; TiFe; $CaNi_5$; $ZrMn_2$

1. Introduction

Hydrogen storage compounds such as $LaNi_5$ and Mg_2Ni are some of key materials for the development of future clean energy system. In order to improve their hydrogen absorption and desorption characteristics the effect of alloying has been investigated experimentally [1]. The electronic structures have also been calculated theoretically [2,3]. However, despite great effort, the alloying effect still remains unclear. For this reason, current alloy design is performed in most cases relying on several empirical rules.

Recently, Yukawa et al. [4] have investigated the alloying effect on the electronic structure of the hydrogenated $LaNi_5$, and have shown that the hydriding properties are well understood in terms of the nature of the chemical bond between atoms in a small octahedron in which the absorbed hydrogen atom is located. In this calculation, alloying elements are substituted for the Ni atoms at the 2c site in the crystal with the P6/*mmm* space group. This 2c site is the first-nearest-neighbour site form the hydrogen atom. In addition to this site, there is another Ni atom site, i.e., the 3g site in the crystal. This is the second-nearest-neighbour site from the hydrogen atom. Any Ni-substitution alloying elements occupy both the 2c and the 3g sites. For example, it is reported that the occupancy numbers of Co in $LaNi_4Co$ are 23% at the 2c site and 77% at the 3g site [5]. Similar results are also obtained for other alloying elements [5].

In the present study, the alloying elements of 3d transition metals, Cr, Fe, Co, Ni and Cu, are substituted for Ni atoms on the 3g site, and the electronic structures are calculated by the DV-Xα molecular orbital method. The results are compared with those previously calculated on the 2c site [4].

2. DV-Xα cluster method and cluster model

The DV-Xα cluster method is a molecular orbital method, assuming a Slater's Xα potential. The detailed explanation of this calculation method is given elsewhere [4].

The cluster model used is shown in Fig. 1, which is constructed on the basis of the crystal structure of α-$LaNi_5H_x$ ($x<0.4$). A hydrogen atom occupies the 3f site in the crystal with the P6/*mmm* space group. That is a central site of the octahedron with the frame of four Ni atoms and two La atoms. In order to examine alloying effects on the electronic structures, two Ni atoms on the 3g site (Ni(2) atoms in Fig. 1) are substituted for various alloying elements, M, (M=Cr, Fe, Co, Ni and Cu). Therefore, the cluster model is expressed as $HM_2La_2Ni_{10}$. Here, any lattice expansion due to the hydrogenation is not taken into account since in the present calculation we aim to obtain a general trend of the change in the chemical bond strength with alloying elements.

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0925-8388/97/$17.00
PII S0925-8388(96)03065-4

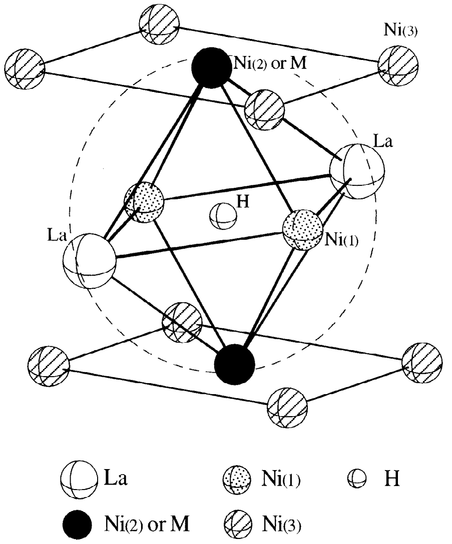

Fig. 1. Cluster model used in the calculation.

3. Results

3.1. Bond order between atoms

The bond order is the overlap population of the electrons between atoms. This is a measure of the strength of the covalent bond between atoms. The calculated bond orders are shown in Fig. 2. Every bond order shown in this figure is the value per atomic bond in the cluster. In Fig. 2(a), the bond order between the hydrogen atom and the La atom is always negative, irrespective of alloying elements, indicating that there is a repulsive interaction operating between them. On the other hand, the bond order between the hydrogen atom and the Ni atom is large and positive. It is evident from these results that the hydrogen atoms make a strong chemical bond with Ni atoms rather than La atoms, in agreement with the previous result [4].

Fig. 2(b) shows the bond orders between the metal–metal pairs in the cluster. Compared to the La–Ni(1) bond order, there are larger changes in the M–Ni(1) and the La–M bond orders with M, both of which are the bond orders between the metal–metal pairs in the octahedron as circled by dotted lines in Fig. 1.

3.2. Ionicities

In addition to the covalency, the charge transfer will contribute to the chemical bond between atoms. The ionicities of each atoms in the cluster are estimated according to the Mulliken population analysis. The results are shown in Fig. 3. As shown in this figure, there is a large change in the ionicity of the alloying element, M. For example, it changes from about +0.08 for Cr to about −0.15 for Ni, following the electronegativity change with M. In response to this change, the ionicity of the La atom also changes slightly, but in the reverse way. On the other hand, the ionicities of the hydrogen atom and the Ni atom are less dependent on M, although they always take negative values. These results indicate that the alloying may yield a very small modification in the chemical bond between the hydrogen and the surrounding atoms from the view of charge transfer.

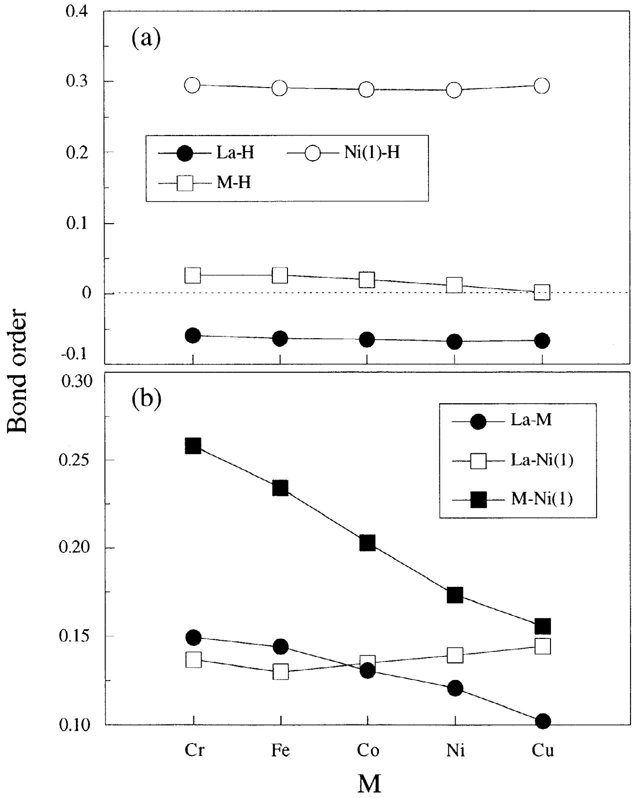

Fig. 2. Changes in the bond orders with the Ni substitutional elements in the $LaNi_5$ system; (a) H–metal bond orders and (b) metal–metal bond orders.

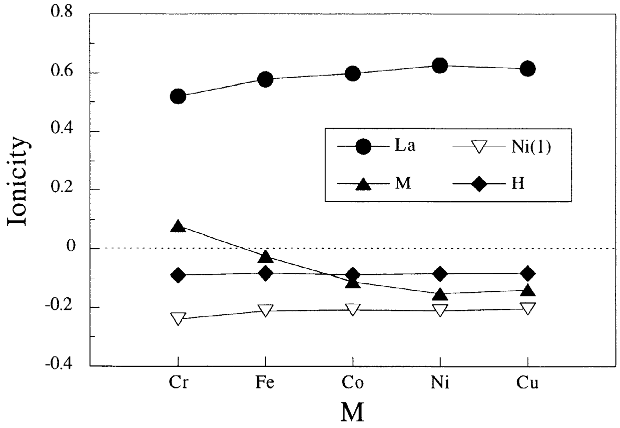

Fig. 3. Changes in the ionicities with the Ni substitutional elements in the $LaNi_5$ system.

4. Discussion

The change in the equilibrium hydrogen pressure at 313 K with alloying elements (M), obtained by Van Mal et al. [1] are shown in Fig. 4. These experimental data are interpreted by using the bond orders between atoms in the cluster.

As shown in Fig. 2(a), the bond orders between the metal–hydrogen pairs in the cluster scarcely change with alloying. On the other hand, as shown in Fig. 2(b), both the La–M and M–Ni(1) interactions in the octahedron change greatly with alloying elements, M. These atomic interactions are supposed to be strong enough to hold the framework of the octahedron. According to the previous calculation [2], the Ni–Ni interaction is reduced by the hydrogenation, but it is recovered to some extent by introducing a small expansion to the Ni atomic plane neighbouring the hydrogen atom. However, as pointed out in our previous study [4], such a recovery is difficult if the La–Ni interaction is significantly large. This is because, as is evident from the atomic arrangements in the octahedron shown in Fig. 1, the La–Ni interaction acts to suppress such a lattice expansion on the Ni atomic plane, so that the Ni(or M)–Ni bond order never recovers resulting in the remarkable reduction in the total chemical bond strengths in the octahedral framework by the hydrogenation. As a result, the stability of the hydride is expected to decrease with increasing La–Ni bond order and with decreasing Ni(M)–Ni bond order. Therefore, the ratio of the bond orders (Bo), defined as Bo(La–Ni)/Bo(M–Ni), is an indication to show the instability of the hydride. The calculated bond order ratios are shown in Fig. 5(a). For comparison, the results for the Ni(2c) substitution [4] are also shown in Fig. 5(b). When compared these results shown in Fig. 5 with the hydrogen desorption pressure shown in Fig. 4, it is found that the bond order ratios are approximately similar to the experimental results regardless of the Ni(3g) or the Ni(2c) substitutions, although there is a small discrepancy between them in the case of the Cu substitution.

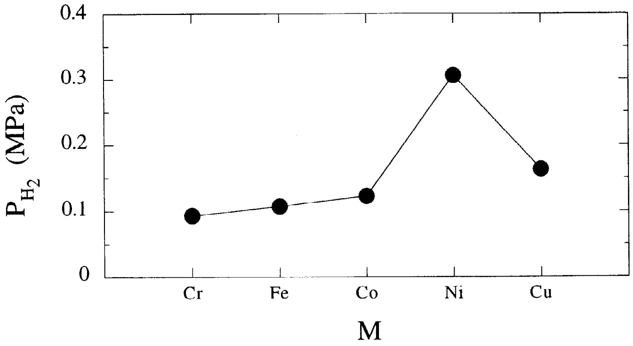

Fig. 4. Equilibrium plateau pressures at 313 K for $LaNi_4M$ [1].

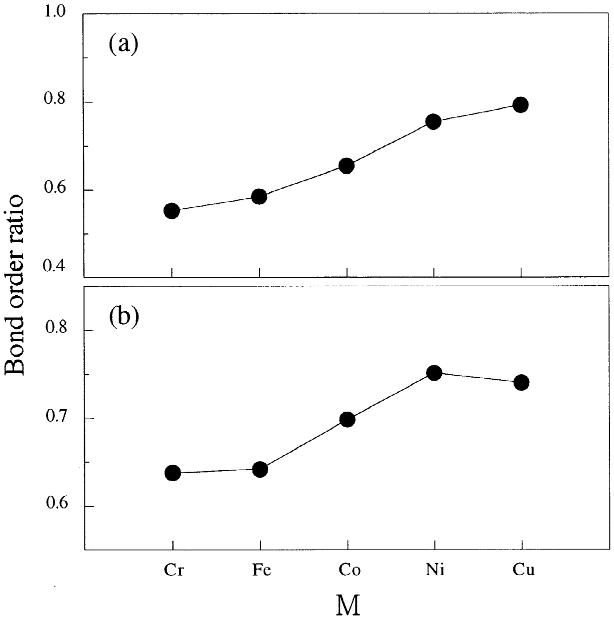

Fig. 5. Changes in the bond order ratios with alloying elements; (a) Ni(3g) substitutions and (b) Ni(2c) substitutions.

This approach is applicable not only to Ni substitution, but also to La substitution [4]. In addition, the same approach is valid in the other system, $CaNi_5$, TiFe and $ZrMn_2$ [7]. The Mg_2Ni system has a rather different chemical bond nature from these systems. However, still the phase stability of the Mg_2Ni_4 hydride is associated with the balance in the chemical bond strength between atoms in a small cube, consisting of a central Ni atom, surrounded by 8 Mg atoms and some hydrogen atoms [6].

5. Conclusion

The hydrogen absorption and desorption characteristics of $LaNi_5$ are well understood in terms of the nature of the chemical bond between atoms in a small octahedron in which the absorbed hydrogen atom is located. The present molecular orbital approach is also useful in understanding experimental results of other hydrogen storage compounds, Mg_2Ni [6], $CaNi_5$, TiFe and $ZrMn_2$ [7].

Acknowledgments

The authors acknowledge the Computer Center, Institute for Molecular Science, Okazaki National Institutes for the use of the SX-3/34R computer. This research is supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Sports, Science and Culture of Japan.

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