Relation between electronic structures of $RENi_5$ and their hydrogen absorption properties

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Since $LaNi_5$ has a storage capacity which is even larger than liquid or solid hydrogen in density, absorbing hydrogen at suitable temperatures and pressures, and can be easily activated, it has been regarded as one of the most important alloys for storing hydrogen so far. As pure La is very expensive, mischmetal (Mm) (99% are La, Ce, Pr, and Nd) usually serves as a substitute for it. According to refs. [1—3], this substitution, especially for Ce, induces a great reduction in the stability of hydride, a tremendous increase in hydrogen vapor pressure by more than tens of times, and also a decrease in the activation ability. Considering that as their atomic structures are similar, they have almost the same atomic radii, it is impossible to interpret the difference in properties by the difference in their atomic radii and structures. But one might easily understand this discrepancy by the difference in their electronic structures. However, there is no report about the calculation of electronic structure of $RENi_5$ so far. Especially, the relation between electronic structures of $RENi_5$ and their hydrogen absorption behavior is still unclear.

This paper calculates the electronic structure of $RENi_5$ (RE=La, Ce, Pr, and Pr) using self-consistent-field-X α-scattered-wave method (SCF-X α-WS)[4], and studies the relation between electronic structure and hydrogen absorption. Some results are interesting and are in agreement with the experimental.

Table 1 Parameters used for calculations and experimental data of hydrogen absorption plateau pressure (P_H)[2]

	a/nm	c/nm	Electronic configurations of RE, Ni	$P_H/10^5$MPa
La_2Ni_4	0.5019	0.3984	$5s^2\,5p^6\,5d^1\,6s^2$, $3d^8 4s^2$	3
Ce_2Ni_4	0.4886	0.4003	$5s^2\,5p^6\,4f^2\,6s^2$, $3d^8\,4s^2$	40
Pr_2Ni_4	0.4967	0.3980	$5s^2\,5p^6\,4f^3\,6s^2$, $3d^8\,4s^2$	12
Nd_2Ni_4	0.4954	0.3978	$5s^2\,5p^6\,4f^4 6s^2$, $3d^8\,4s^2$	13

1 Calculation method and model

SCF-Xα-WS method has been proven to be a maturated and perfect calculation method of quantum mechanics, and a powerful tool for solving a cluster of multiple atoms. Its main idea is the following: For a cluster system, make an approximation such that Xα potential is in statistical mean and also make a Muffin-tin approximation to divide the cluster into three regions. In the three regions, based on the energy coordinations of multiple-wave functions and the continuous condition at each boundary, slove their equations, and give out their energy engenvalues, state functions, self-consistent potentials, Hellmann-Feynman (HF) forces and some other parameters.

Using the characteristics of SCF-Xα-WS method, we select a typical RE_2Ni_4 octahedral cluster to represent the $RENi_5$, as shown in fig. 1. This cluster includes all of the three kinds of atoms (Ni1, Ni2 and RE) with its center position occupied by a majority of the hydrogen atoms, so that it is easy to study the relationship between the electronic structures and the hydrogen absorption properties. Table 1 lists the configurations of outer-shell electrons of RE and Ni, and the lattice parameters of $RENi_5$ taken from ref. [2]. When the calculation is self-consistent, the maximum of relative change in potential is smaller than 1.0×10^{-5} (the threshold value).

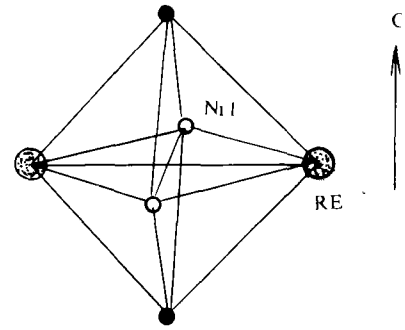

Fig. 1. Model for Re_2NiO_4.

2 Results and discussion

Table 2 lists the results on FH force, total energy (E_{tot}), Viril coefficient, Fermi energy level (E_f) and the energy level above E_f(E_{f+}). In this study, the Viril coefficients of four clusters are all larger than 0.99977. In the light of the distributions of energy levels, the relationship between the electronic structures of $RENi_5$ and their hydrogen absorption properties is studied.

Table 2 Results of calculations

	E_{tot}(Ry×10⁴)	Viril coef.	E_f(Ry)	E_{f+}(Ry)	Hellmann-Feynman (a.u.)		
					RE-RE	RE-Ni1	RE-Ni2
La_2Ni_4	−4.492	0.999 94	−0.318 1	−0.264 6	0.611	2.668	3.099
Ce_2Ni_4	−4.631	0.999 86	−0.176 2	−0.160 8	1.034	2.893	2.225
Pr_2Ni_4	−4.771	0.999 77	−0.228 7	−0.209 1	2.736	3.560	0.579
Nd_2Ni_4	−4.895	0.999 88	−0.246 6	−0.232 8	1.723	2.544	1.079

(1) Usually it was thought that the contribution of RE to the coupling comes from the outer-shell electrons of uncompleted shell 4*f* and 6*s*. This calculation indicates that the

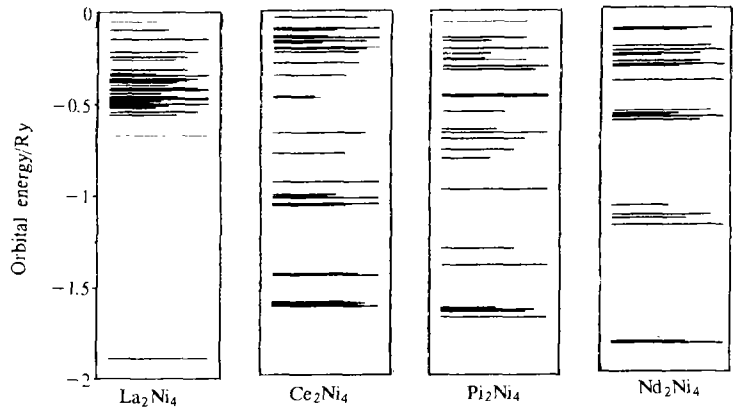

Fig. 3. Diagrams of orbital energy level of Re_2Ni_4.

the calculation between results of 6-atom cluster of this study and that of a large cluster with more atoms.

(3) Calculation results (table 2) show that all the HF force is center forward. After La is replaced by Ce, Pr and Nd, the HF force of RE-RE almost gets doubled, the force of RE-Ni1 increases a little or keeps constant, but the HF force of RE-Ni2 decreases a lot. Therefore after La is replaced, on the plane vertical to the *c*-direction, the coupling between atoms is enhanced greatly, but in the direction of *c*, the coupling between atoms is weakened. All of the coupling force has not be enforced. Comparison of the ratio of two HF forces shows that the anisotropies of the La and Pr clusters are smaller than that of the Ce and Pr clusters. Therefore, the replacement of La by Ce and Nd increases E_f, and at the same time decreases the anisotropy of $RENi_5$, thus exerting some influence on the hydrogen absorption properties.

3 Summary

In this paper, using SCF-Xα-WS method, the electronic structures of RE_2Ni_4 clusters (RE=La, Ce, Pr, and Nd) are calculated. The results show that: (i) both electrons on complete shells of 5*s* and 5*p* of RE, and the electrons on uncompleted shells contribute to the coupling between RE and other atoms, which plays an important role in stabilizing the structure; (ii) E_f has a close relationship with the hydrogen absorption plateau pressure: the lower the energy level of E_f, the better the stability of hydride and the smaller the hydrogen absorption plateau pressure; (iii) after Ce, Pr, and Nd replace La, the coupling between atoms increases greatly on the plane vertical to the *c*-direction but decreases a little in the *c*-direction.

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