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First-principles study of a hydrogen storage material CaSi

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We report the results of the first-principles calculation on the hydrogen storage material CaSi. The stability and bonding nature of CaSi hydride have been investigated theoretically with the ultrasoft pseudopotential method based on the density functional theory before experimentation. Theoretical prediction has suggested that CaSi hydride is thermodynamically stable. In actual measurements [M. Aoki *et al.*, Appl. Phys. Lett. **85** 387 (2004)] it is confirmed that CaSi reversibly absorbs and desorbs hydrogen, and the maximum hydrogen content is 1.9 wt % which means CaSi forms $CaSiH_{1.3}$. The hydriding reaction enthalpy of $CaSiH_{1.3}$ is estimated as -42 kJ/mol H_2 from the calculation based on the crystal structure symmetry determined by the Rietveld refinements of synchrotron x-ray diffraction data, which is in fairly good agreement with an experimental value of -62 kJ/mol H_2. From the calculation results of density of states, $CaSiH_{1.3}$ has an energy gap of 0.013 eV and the electronic structure is nonmetallic. The charge-density distribution indicates that one Si atom and one H atom are bonding covalently. It is thought that these electronic structures cause the stability of $CaSiH_{1.3}$.

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I. INTRODUCTION

Hydrogen is considered to be one of the most promising clean energy sources with the capability of replacing fossil fuels. The use of hydrogen-based energy in practical applications such as fuel cell vehicles, however, requires the development of safe and efficient hydrogen storage technology. Although metal hydrides are considered to be among the promising materials for hydrogen storage, those developed so far do not possess sufficient gravimetric hydrogen storage capacity for practical applications. Accordingly, the development of new hydrides of light metals possessing large hydrogen storage capacities is strongly desired.

It is well known that ZrNi with the CrB-type structure (space group *Cmcm*) absorbs a large number of hydrogen atoms per metal atom and forms $ZrNiH_3$.[1–4] Other alloys with the same structure are also expected to have large hydrogen storage capacities. Therefore, we turn our attention to CaSi (Refs. 5 and 6) which has the CrB-type structure, since its average atomic weight is 34 and it consists of Ca and Si which are much lighter elements than Zr and Ni. In addition, Ca and Si have the advantage of being low-cost elements compared with the existing hydrogen storage materials in which rare metals such as Ni and La are used.

In exploring new hydrogen storage materials, hydriding experiments have been carried out with no certainty that a new hydride would actually be formed. On the other hand, recently some first-principles studies on existing metal hydrides and alkali complex hydrides have been performed,[7–12] and it has been reported that these calculations predict with sufficient accuracy characteristics such as formation enthalpy of hydrides. If theoretical calculation can predict whether a new hydride is generated in advance, more efficient development of hydrogen storage materials is attained. Thus, we have performed first-principles calculations to predict the hydriding properties of CaSi first, and then we have conducted an experiment to investigate these properties with some certainty based on the theoretical predictions. Consequently, hydrogen storage material CaSi has been developed.[13]

This paper is mainly organized around the theoretical results of the CaSi hydride using first-principles calculations. In Sec. II, we describe the details of the computational method. Section III reports the theoretical predictions for the stability of CaSi hydride in which hydrogen is put on the same site as other CrB-type hydrides. Comparison with the experimental results and theoretical predictions is also discussed. Furthermore, we show the calculation results on the structural parameters and electronic structures for actual CaSi hydride investigated by experiment. Finally, this study is summarized in Sec. IV.

II. COMPUTATIONAL DETAILS

First-principles calculations have been performed by the ultrasoft pseudopotential method[14] based on the density functional theory.[15] The generalized gradient approximation (GGA) formula[16] is applied to the exchange-correlation energy.

The interaction between the ion cores and electrons is described by the norm-conserving pseudopotential[17] for Si and by the ultrasoft pseudopotential[14] for Ca and H. In a pseudopotential generation scheme, the pseudo-wave-functions and the pseudo-charge-augmentation functions are optimized by a method similar to that proposed by Rappe *et al.*[18] We chose 3*s*, 3*p*, 3*d*, 4*s*, 4*p*, and 4*d* states for Ca pseudopotential as the reference states; 3*s*, 3*p*, and 3*d* states for Si; and 1*s*, 2*s*, and 2*p* states for H, respectively. Moreover, the partial core correction[19] is taken into account for Ca and Si pseudopotentials.

In the solid-state calculations, the pseudo-wave-functions are expanded by plane waves with a cutoff energy equal to 15 hartrees. The cutoff energy for the charge density and potential is set to be 120 hartrees. The integral over the Brillouin zone for the CrB-type crystal structure is approximated by the summation on an $18\times6\times8$ Monkhorst-Pack[20]

TABLE I. Structural parameters of CaSi with the CrB-type structure (space group *Cmcm*).

	Lattice constants (Å)		
	a	*b*	*c*
Calculation[a]	4.517	10.725	3.886
Experiment[b]	4.561	10.735	3.891
Experiment[c]	4.545	10.728	3.890
Experiment[d]	4.559	10.725	3.893

Internal parameters

	Atom	Site	x/a	y/b	z/c
Calculation[e]	Ca	4*c*	0	0.3605	0.25
	Si	4*c*	0	0.0688	0.25
Experiment[f]	Ca	4*c*	0	0.3587	0.25
	Si	4*c*	0	0.0691	0.25
Experiment[g]	Ca	4*c*	0	0.367	0.25
	Si	4*c*	0	0.108	0.25

	Enthalpy of formation (kJ/mol atoms)
Calculation[h]	−61.5
Experiment[i]	−49.6

[a] This work
[b] Reference 5
[c] Reference 6
[d] Reference 13
[e] This work
[f] Reference 26
[g] Reference 6
[h] This work
[i] Reference 27

k-point mesh, and similar quality of **k**-grid density is used for other crystal structures. The preconditioned conjugate-gradient technique is employed to minimize the Kohn-Sham energy functional. A procedure based on the iterative diagonalization scheme[21] and the Broyden charge-mixing method[22] is adopted in the present study. Optimization of crystal structures is performed so that the atomic forces and the macroscopic stresses are less than 5×10^{-4} hartree/bohr and 0.1 GPa, respectively. During the structural optimization process, the partial occupation numbers near the Fermi level are determined by the Fermi-Dirac distribution function with $k_BT=3\times10^{-3}$ hartrees, and the Helmholtz free-energy functional,[23] including the entropy term, is minimized instead of the Kohn-Sham energy functional. Then, the improved tetrahedron method[24] is used in order to minimize the Kohn-Sham energy functional in the optimized structure.

III. RESULTS AND DISCUSSIONS

A. Theoretical prediction for the stability of CaSi hydride

First, we have computed for the CrB-type CaSi which is the starting material for hydriding reaction. The optimized lattice constants and atomic positions of CaSi are shown in Table I. The calculation values are in good agreement with the experimental ones,[5,6,13] and it is confirmed that our calculation has sufficient accuracy. The cohesive energy of CaSi is 3.8134 eV/atom, which agrees very well with the reported value of 3.882 eV/atom computed by the linear muffin-tin orbital (LMTO) method.[25] Table I also gives a comparison of the theoretical and experimental values[27] of enthalpy of formation for the CaSi compound. Both agree well if the difference of temperature (the theoretical value at absolute zero temperature and the experimental one at 298 K) is taken into consideration.

In the present calculations for CaSi hydride, hydrogen content and positions are assumed to be the same as ZrNiH (H is put on the 4*c* site surrounded by four Ca atoms of the *Cmcm* space group[1]) and $ZrNiH_3$ (the 4*c* site surrounded by three Ca and two Si atoms and the 8 f site surrounded by three Ca and one Si atoms of *Cmcm* space group[1,2]). Although the triclinic crystal structure model is also reported in ZrNiH, the deformation of lattice is very small. Similarly, we have also calculated CaSiH with the triclinic crystal structure, and it is confirmed that there is hardly a deformation of lattice or a difference of energy between the two.

The structure model of CaSiH is shown in Fig. 1. For the optimized structures of CaSiH and $CaSiH_3$, the calculated

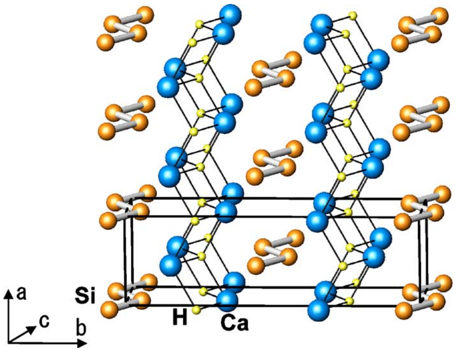

FIG. 1. (Color online) Crystal structure model of CaSiH. Large, middle, and small spheres denote Ca, Si, and H atoms, respectively.

cohesive energies are 3.3455 eV/atom and 2.7825 eV/atom, respectively.

The enthalpy of hydride formation is obtained by subtracting the cohesive energies of CaSi and the hydrogen molecule from that of CaSi hydride. The calculation for the hydrogen molecule has been performed using a cubic supercell with size of $6 \times 6 \times 6$ Å^3. The bond length and the binding energy are predicted to be 0.755 Å and 4.536 eV/H_2, respectively, which agree with the experimental values of 0.741 Å (Ref. 28) and 4.747 eV/H_2.[29] The enthalpies of formation for CaSiH and $CaSiH_3$ obtained by this calculation are −27 kJ/mol H_2 and +33 kJ/mol H_2, respectively, where the effects of the zero-point energy are not taken into consideration. Although the value of the enthalpy for $CaSiH_3$ is positive, that for CaSiH is negative. These theoretical predictions suggest that CaSi absorbs hydrogen and forms CaSi hydride (CaSiH).

Figure 2 shows the total and partial density of states (DOS) for CaSiH, which denotes that its electronic structure is metallic. Since the H atoms exist near the Ca atoms rather than the Si atoms, the H states are localized in the same region as the Ca states.

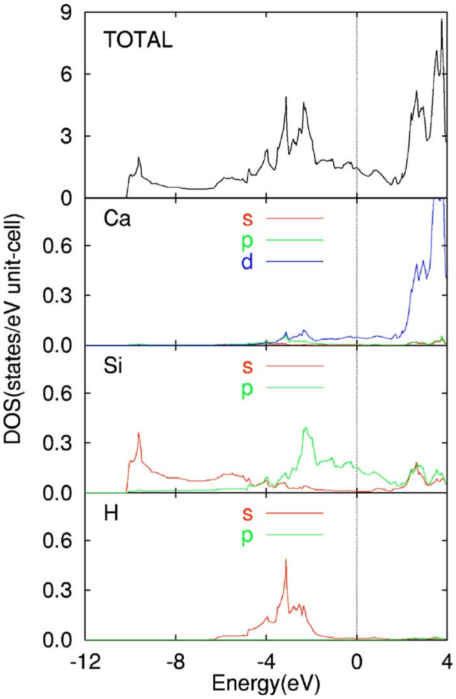

FIG. 2. (Color online) The total and partial densities of states (DOS) for CaSiH. The energy is measured in eV relative to the top of valence states.

B. Comparison with experiment

Encouraged by the theoretical prediction in the preceding section, we have conducted the experiment to investigate the hydriding and dehydriding properties of CaSi. The experimental details are reported in Refs. 13 and 30. In a nutshell, CaSi reversibly absorbs and desorbs hydrogen, and the maximum hydrogen content at 473 K under 9 MPa of hydrogen pressure is 1.9 wt %, which means that CaSi forms $CaSiH_{1.3}$. Moreover, the enthalpy of hydride formation estimated using a van't Hoff plot of plateau pressure is −62 kJ/mol H_2.

Thus in actual experiment, it is confirmed that CaSi absorbs hydrogen, but there are some discrepancies between the predicted and experimental values of the maximum hydrogen content and the enthalpy of hydride formation. We think that the crystal structure of CaSi hydride causes these differences. The crystal structure of $CaSiH_{1.3}$ phase is different from those of ZrNiH and $ZrNiH_3$,[1–4] because the x-ray diffraction (XRD) spectra of $CaSiH_{1.3}$ shown in Fig. 3(b) of Ref. 13 indicate neither the orthorhombic (or triclinic) lattice found in the ZrNiH phase nor the orthorhombic *Cmcm* symmetry as in $ZrNiH_3$. On the other hand, hydrogen is put on the same site as ZrNiH and $ZrNiH_3$ in our calculations for CaSiH and $CaSiH_3$, respectively. Further, the detailed structure of CaSi hydride has been investigated by precise XRD measurement using synchrotron radiation, which is a high-intensity x-ray source. The synchrotron XRD profiles suggest that the space group of CaSi hydride is *Pnma* (No. 62).[31] This has an orthorhombic symmetry, and the unit cell is three times as long as that of the CrB-type CaSi along the *a* axis as shown in Fig. 3. Then, the recalculation of CaSi hydride has been performed based on the crystal structure symmetry of $CaSiH_{1.3}$ determined by Rietveld refinements of synchrotron XRD data.

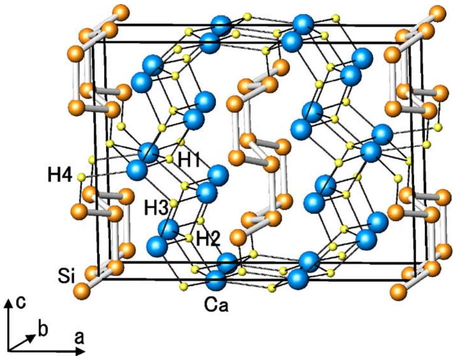

FIG. 3. (Color online) Crystal structure of $CaSiH_{1.3}$ with space group *Pnma*. Large, middle, and small spheres denote Ca, Si, and H atoms, respectively.

TABLE II. Structural parameters of $CaSiH_{1.3}$ obtained from experiment and calculation. The space group is *Pnma* (No. 62).

Atom	Site	x/a	y/b	z/c	Occupation factor
Experiment[a]: $a=14.545(3)$ Å, $b=3.8198(7)$ Å, $c=11.226(2)$ Å					
Ca1	4*c*	0.3625(1)	1/4	−0.0185(2)	1.0
Ca2	4*c*	0.1918(1)	3/4	0.1597(2)	1.0
Ca3	4*c*	0.3369(1)	1/4	0.3492(2)	1.0
Si1	4*c*	0.0453(1)	1/4	0.0325(3)	1.0
Si2	4*c*	0.4569(2)	3/4	0.1877(2)	1.0
Si3	4*c*	0.5423(2)	1/4	0.2462(2)	1.0
H1	4*c*	0.248(2)	3/4	−0.023(6)	1.0
H2	4*c*	0.242(3)	1/4	0.163(7)	1.0
H3	4*c*	0.250(3)	3/4	0.346(7)	1.0
H4	4*c*	0.027(3)	1/4	0.524(5)	0.8(1)
Calculation: $a=14.5603$ Å, $b=3.8272$ Å, $c=11.0495$ Å					
Ca1	4*c*	0.3608	1/4	−0.0217	
Ca2	4*c*	0.1962	3/4	0.1571	
Ca3	4*c*	0.3392	1/4	0.3476	
Si1	4*c*	0.0451	1/4	0.0324	
Si2	4*c*	0.4531	3/4	0.1960	
Si3	4*c*	0.5467	1/4	0.2417	
H1	4*c*	0.2771	3/4	−0.0114	
H2	4*c*	0.2785	1/4	0.1571	
H3	4*c*	0.2517	3/4	0.3403	
H4	4*c*	0.0371	1/4	0.5533	

[a]Reference 31.

C. $CaSiH_{1.3}$

The structural parameters of $CaSiH_{1.3}$ obtained from the structure-optimizing calculation are shown in Table II with the experimental data determined by the synchrotron XRD profiles.[31] Although the experimental occupancy of the H4 atom is less than 1.0, those of all hydrogen atoms are set to 1.0 in the present calculation. The structural parameters obtained from this calculation and experiment are very similar to one another except for the atomic positions of H1 and H2 atoms. We have also calculated fixing the experimental values for the configurations of atoms and the lattice constants, provided that all occupancies of hydrogen atoms are set to 1.0, but the energy is 0.034 eV/atom higher than the most stable calculated structure. So, the discrepancy between the experiment and calculation is considered to originate in the occupancy probabilities of H atoms. Therefore, if the calculation taking the fractional occupancy of H atoms into consideration is performed, this discrepancy will be lessened. In this connection we will systematically investigate the detailed structure of CaSi deutride by neutron diffraction measurement as well.

The cohesive energy of the most stable computed structure for $CaSiH_{1.3}$ is 3.2828 eV/atom. Based on this, the enthalpy of hydride formation is estimated as −42 kJ/mol H_2, which is not including the zero-point energy. The formation enthalpy for $CaSiH_{1.3}$ is more negative than that for CaSiH reported in Sec. III A (−27 kJ/mol H_2) and closer to the experimental value (−62 kJ/mol H_2). It is also confirmed from calculation that not CaSiH but $CaSiH_{1.3}$ is formed as the CaSi hydride. Regarding the enthalpy of hydride formation, it is also reported that the computed value for MgH_2 is an underbinding of 20 kJ/mol H_2 as compared with the experimental value.[9] Consequently the theoretical enthalpy value of $CaSiH_{1.3}$ is in fairly good agreement with the experimental one. It is thought that one of the causes of this difference is the fractional occupancy of H atoms, too. When we performed the calculation on $CaSiH_{1.25}$ such that one hydrogen atom among four H4 atoms in unit-cell of $CaSiH_{1.3}$ was removed by way of trial, the formation enthalpy value of hydride became lower than that of $CaSiH_{1.3}$ by 2 kJ/mol H_2 although it fell short of a quantitative agreement with the experiment. In addition, concerning the hydrogen-metal system, there are reports that the local motion of hydrogen atoms should be treated quantum mechanically.[32,33] It will be necessary to do the calculation taking such an effect into consideration in future in order to make the discrepancy between theoretical and experimental values of enthalpy of formations lessen.

The total and partial densities of states (DOS) for $CaSiH_{1.3}$ are shown in Fig. 4. The $CaSiH_{1.3}$ has an energy gap of 0.013 eV and its electronic structure is nonmetallic. Since it is well known that the value of the calculated energy-gap underestimates the experimental one, the actual

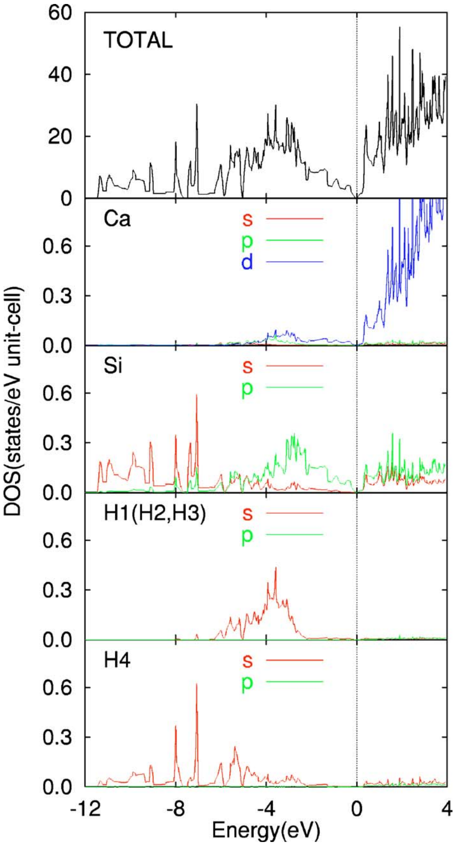

FIG. 4. (Color online) The total and partial densities of states (DOS) for $CaSiH_{1.3}$. The energy is measured in eV relative to the top of valence states.

energy gap value of $CaSiH_{1.3}$ will be larger. Such a behavior as the energy gap of $CaSiH_{1.3}$ is also measured by nuclear magnetic resonance (NMR) spectroscopy.[34] Compared with Fig. 2, each Ca and H1 (H2, H3) state is distributed similarly, while valence bandwidth of the Si state becomes wider reflecting the hybridization of the states of H4 and Si. Moreover, although CaSiH has no energy gap, $CaSiH_{1.3}$ has the energy gap, and the nonmetallic electronic structure of $CaSiH_{1.3}$ seems to stabilize it more.

In order to understand the bonding nature of $CaSiH_{1.3}$ in more detail, the charge-density distribution has been investigated. Figure 5 shows the contour plot of charge densities of $CaSiH_{1.3}$ on (040) plane, which include the partial core corrections for Ca and Si. It is also confirmed that the Si2 and H4 atoms are bonding covalently; this bonding feature resembles well that of the silane molecule (SiH_4). The interatomic distance of Si2—H4 atoms is 1.58 Å, which is close to the bond length of SiH_4 (1.48 Å).[35] The coordination number of Si atoms is usually four, so the Si1 and Si3 atoms are bonded with three nearby Si atoms, respectively. On the other hand, since the number of nearest-neighbor Si atoms of Si2 is two, the H4 atom exists near the Si2 atom and they are bonding covalently with each other. Concerning the fourth bond, it is considered that all Si atoms have charge transfer from Ca. In addition, charge transfer from the Ca atom is also done to H1, H2, and H3, because of the small contribution of the Ca orbit for occupied states indicated by the partial density of state of Fig. 4 and the relatively high charge-density distributions (Fig. 5) around the H1, H2, and H3 atoms existing near the Ca atom. Therefore it is expected that Ca atoms are ionized as Ca^{2+} cations and H1, H2, and H3 atoms become like H^- anions. These charge transfers and the covalent bonding between Si2 and H4 atoms cause the change in the band structure of $CaSiH_{1.3}$.

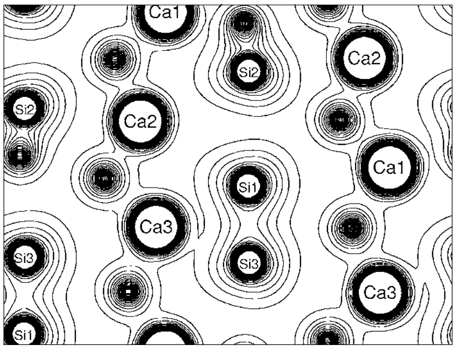

FIG. 5. The charge-density distribution of $CaSiH_{1.3}$ on (040) plane. The contour lines are plotted within 0.0~2.0 e/Å at 0.1 e/Å intervals.

IV. SUMMARY

We have performed first-principles calculations to investigate the hydriding properties of CaSi first. The theoretical predictions of CaSi hydride in which hydrogen is put on the same site as other CrB-type hydrides suggest that the CaSi hydride (CaSiH) is thermodynamically stable. In actual experiment, it is confirmed that CaSi absorbs hydrogen, but as compared with calculated results, there are some discrepancies of the maximum hydrogen content and the enthalpy of hydride formation. Then, the recalculation of CaSi hydride has been performed based on the crystal structure parameters of $CaSiH_{1.3}$ determined by Rietveld refinements of synchrotron XRD data.

The most-stable calculated structural parameters agree with experimental values except for the atomic positions of the H1 and H2 atoms. Moreover, the enthalpy of hydride formation obtained by subtracting the energies of CaSi and the hydrogen molecule from that of the hydride thereof which is calculated to be the most stable structure of $CaSiH_{1.3}$ is estimated as $-42\ \mathrm{kJ/mol\ H_2}$ without the zero-point energy, and this computed value is almost in agreement with the experimental one ($-62\ \mathrm{kJ/mol\ H_2}$). We think that these discrepancies will be lessened if the calculation in consideration of the fractional occupancy of H atoms and/or the quantum-mechanical motion of hydrogen atoms is performed.

The hydrogen content of 1.9 wt % for CaSi is inadequate for practical use as a hydrogen storage material. Therefore, we have investigated the detailed electronic structure of CaSi hydride in order to improve its performance. The $CaSiH_{1.3}$ has an energy gap of 0.013 eV and its nonmetallic electronic structure seems to cause the stability of $CaSiH_{1.3}$. From the charge-density distributions, it is confirmed that the Si2 and H4 atoms are bonding covalently. This bonding feature resembles well that of the silane molecule (SiH_4). In addition, there are charge transfers from Ca to all Si and H1, H2, and H3 atoms. These charge transfers and the covalent bonding of Si2—H4 atoms cause the change in the band structure of $CaSiH_{1.3}$. In order to increase hydrogen content of $CaSiH_{1.3}$ more, we are investigating the validity of the substitution of the Si atom, because the space into which more hydrogen atoms are inserted seems likely to be the site near the Si atoms.

This study reports on hydrogen storage material development based on the theoretical predictions, and it is expected that such a development technique using first-principles calculations will greatly aid exploration of other hydrogen storage materials.

Finally, it is noted that the reversible hydriding and dehydriding properties of CaSi suggest a great potential of metal silicides for hydrogen storage. Since silicon is the second-most-abundant element in the Earth's crust, the hydrogen storage materials of silicides such as CaSi have the great advantage of being low cost. We are also studying the hydriding and dehydriding properties of other metal silicides by the development technique which combines theoretical predictions and experiments.

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