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Structure and Hydrogen Bonding in CaSiD$_{1+x}$: Issues About Covalent Bonding

Hui Wu
National Institute of Standards and Technology; University of Maryland

Wei Zhou
National Institute of Standards and Technology; University of Pennsylvania

Terrence J. Udovic
National Institute of Standards and Technology

John J. Rush
National Institute of Standards and Technology; University of Maryland

Taner Yildirim
National Institute of Standards and Technology; University of Pennsylvania, taner@seas.upenn.edu

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Structure and hydrogen bonding in CaSiD$_{1+x}$: Issues about covalent bonding

H. Wu,1,2,* W. Zhou,1,3 T. J. Udovic,1 J. J. Rush,1,2 and T. Yildirim1,3

1NIST Center for Neutron Research, National Institute of Standards and Technology, 100 Bureau Drive, MS 8562, Gaithersburg, Maryland 20899-8562, USA
2Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742-2115, USA
3Department of Materials Science and Engineering, University of Pennsylvania, 3231 Walnut Street, Philadelphia, Pennsylvania 19104-6272, USA

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We report here our high-resolution neutron powder diffraction and neutron vibrational spectroscopy study of CaSiD$_{1+x}$ along with first-principles calculations, which reveal the deuterium structural arrangements and bonding in this novel alloy hydride. Both the structural and spectroscopic results show that, for $x>0$, D atoms start occupying a Ca$_3$Si interstitial site. The corresponding Si-D bond length is determined to be 1.82 Å, fully 0.24 Å larger than predicted by theory. Thus, our neutron measurements are at odds with the strongly covalent Si-H bonding in CaSiH$_{1+x}$ that such calculations suggest, a result which may have implications for a number of ongoing studies of metal-hydrogen systems destabilized by Si alloying.

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I. INTRODUCTION

Recently there has been hydrogen-storage interest in the intermetallic compound, CaSi, which has been found to reversibly absorb more than one hydrogen per CaSi formula unit.1 While both x-ray diffraction and first-principles calculations have shed light on the general structure of CaSiH$_{1+x}$ (Refs. 1 and 2), no neutron powder diffraction (NPD) or neutron vibrational spectroscopy (NVS) studies have thus far been reported to elucidate the exact interstitial locations and bonding of the H atoms within the rearranged CaSi lattice, and in so doing, rigorously test recent theoretical predictions.2 High-resolution NPD combined with NVS provide a powerful probe of the structure, dynamics, and bonding states in metal-hydride materials. Hence, in the present work, we report our neutron scattering results compared with first-principles phonon calculations for CaSiD$_{1+x}$. The neutron results, particularly our structural study, are not consistent with the strongly covalent Si-H bonding in this system predicted by theory.

II. EXPERIMENTAL SECTION

A CaSiD$_{1.2}$ powder sample was synthesized by (i) first forming CaSi via evacuation of a ball-milled (400 rpm for 30 min) CaH$_2$ (Aldrich,$^3$ 99.9%) + Si (Alfa Aesar 99.999%) 1:1 stoichiometric mixture at 873 K for 5 h, and (ii) deuteriding this CaSi by reaction with gas-phase D$_2$ (99.999%) at 9 MPa and 473 K. CaSiD was obtained by controlled evacuative desorption of D$_2$ from CaSiD$_{1.2}$ at 353–373 K. CaSi, CaSiD, and CaSiD$_{1.2}$ crystal structures were determined using high-resolution NPD. In addition, D optical phonon spectra of CaSiD and CaSiD$_{1.2}$ were measured by NVS. All sample handling was performed in a He-filled glovebox to avoid oxidation reactions.

All measurements were undertaken at the NIST Center for Neutron Research. The NPD measurements were performed with the BT-1 high-resolution powder diffractometer$^4$ using

FIG. 1. (Color online) Experimental (dots), calculated (line), and difference NPD profiles for (a) CaSiD$_{1.2}$ and (b) CaSiD. The low-angle portions of the diffraction patterns are also presented in insets. An additional small inset shows expanded-scale (200) peaks for (a) CaSiD$_{1.2}$ and (b) CaSiD more clearly indicating the peak shift. Squares indicated the positions of some impurity peaks that are not related to the CaSiD$_{1.2}$ and CaSiD phases. These impurity peaks were removed from the NPD patterns for clarity.
the Cu(311) monochromator at a wavelength of 1.5403(2) Å. Rietveld structural refinements were done using the GSAS package. The NVS measurements were performed with the BT-4 filter-analyzer neutron spectrometer using the Cu(220) monochromator.

### III. RESULTS AND DISCUSSION

The effectiveness of the ball-milling method for producing single-phase CaSi was demonstrated by the good agreement between the published CaSi (CrB-type) structure and the refinement model fits of the NPD data collected on the resultant alloy. Structure refinements on CaSiD$_{1.2}$ were performed within the space group $Pnma$ (No. 62) with the initial atomic positions as suggested from the recent calculations of Obba et al. The experimental, fitted, and difference profiles of the NPD patterns for the final refined structures of CaSiD$_{1.2}$ are shown in Fig. 1. The refined atomic positions yield excellent fits for the observed profiles of all the peaks. The final refined crystallographic parameters are summarized in Tables I and II. The results are generally consistent with the recent x-ray diffraction study. No significant structural changes or phase transformations were evident from the difference patterns at 10 K and 298 K. Structure refinement using the NPD data for CaSiD (Fig. 1) also revealed a $Pnma$ unit cell (Tables I and II), which differs from the CrB-type structure of CaSiH (space group $Cmcm$) suggested by Obba et al. From Fig. 1, visible changes in peak intensities [e.g., (101)], shapes [e.g., (312) and (410)], and positions [e.g., (200) and (020)] clearly show structure variations with D concentration (also see the lattice parameter changes in Table II).

#### TABLE I. Crystallographic data for CaSiD$_{y}$ at 298 K.

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<tr>
<th>Space group</th>
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<th>$y=0.97\approx1$</th>
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<td>$Pnma$</td>
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<td>$a$ (Å)</td>
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<td>14.20912(32)</td>
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<td>$b$ (Å)</td>
<td>3.82028(23)</td>
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<tr>
<td>$c$ (Å)</td>
<td>11.20921(12)</td>
<td>11.46781(27)</td>
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<td>$V$ (Å$^3$)</td>
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#### TABLE II. Refined structural parameters for CaSiD$_{y}$ at 298 K.

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<th>Site</th>
<th>Occupancy</th>
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<th>$y$</th>
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<td>1.809(1)</td>
<td>0.462(6)</td>
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<th>Atom</th>
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<th>Occupancy</th>
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<th>$y$</th>
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$^{a}$The D3 occupancy tended to be slightly larger than 1 during the refinement, and was thus fixed at 1.

$^{b}$The D4 occupancy tended to be slightly negative during the refinement, and was thus fixed at 0. $U_{ij}$ are all $\times 100$ Å$^2$. All thermal factors are assumed to be anisotropic and identical for all atoms of the same element.
The structural models indicate that the intensity of the peak increases with increasing D occupancy of the Ca$_3$Si$_D$ site. The refined deuterium occupancies yield stoichiometries of “CaSiD$_{1.19}$” and “CaSiD$_{0.97}$,” respectively, for the CaSiD$_{1.2}$ and CaSiD samples, consistent with the measured gravimetric uptakes for the deuterides.

The refined structures of CaSiD$_{1.2}$ and CaSiD are shown in Fig. 2. For simplicity, anisotropic thermal factors were assumed to be identical for all atoms of the same element. Allowing for the independent refinement of thermal factors for each atom in the unit cell led to similar structural results with only insignificant changes in some of the atomic fractions and no strong correlations between occupancies and thermal factors. Compared to CaSi, the unit cell of CaSiD$_{1.2}$ expands three times along the c axis of CaSi, and the resultant structure has two kinds of D sites with different nearest neighbors. One kind of D site (the D1, D2, and D3 sites), is defined by four Ca nearest neighbors (Ca$_4$ sites, 1 per CaSi). These Ca$_4$ tetrahedra align in a zigzag fashion along the c direction. The Ca-D distances for these sites vary from 2.01 Å to 2.64 Å, in the same range as the Ca-D distances in CaD$_2$.

Interestingly, the D1, D2, and D3 sites do not have identical coordination environments. Rather, they reside in slightly different off-centered positions in the Ca$_4$ interstices.

The second kind of D site (D4) is located close to the center of a triangle of three Ca (Ca$_1$) atoms as well as one Si (Si$_3$) atom (Ca$_3$Si$_1$ site, 0.33 per CaSi). Since CaSiD$_{1.2}$ is a D-deficient CaSiD$_{1.33}$ phase, the D4 sites are found to be partially occupied (59%), presumably in a disordered fashion. The minimum D4-D4 distance is 2.21 Å and the minimum separation between the Ca$_4$ and Ca$_3$Si sites is 3.13 Å. A recent theoretical study of CaSiH$_{1.3}$ by Ohba et al. has concluded that the H atom in the Ca$_3$Si-type site is covalently bonded to the Si atom with a Si-H bond length of 1.58 Å, close to the 1.48 Å bond length in SiH$_4$. Yet, our results indicate that the Si$_3$-D$_4$ distance is 1.82 Å at 298 K, considerably larger (by $\approx$0.24 Å) than that predicted by Ohba et al., and also consistent with the bond length calculated from the atomic positions tabulated by the same authors from synchrotron x-ray data. Figure 3 shows that fixing this Si-D distance at values either increasingly larger or smaller than 1.82 Å leads to increasing $\chi^2$ and $R_{wp}$ values (i.e., poorer model fits). Similar results are found for calculated deviations in other crystallographic directions. Besides being much larger than the Si-H bond length in SiH$_4$, 1.82 Å is also larger than that of any Si-H bond reported for various Si-H cluster, defect, and hydrogenated silicon 1.50–1.56 Å.

These experimental results clearly call into question the prediction of Si-H covalency by first-principles calculations.

The refined structure of CaSiD [Fig. 2(b)] reveals an empty D4 site and essentially full occupancies of the other three Ca$_4$-type D sites in the lattice. Compared to CaSiD$_{1.2}$,
CaSiD retains the Pnma symmetry with a slight shrinkage along the a axis and slight expansions along the b and c axes. Similar to CaSiD₁₂, the D1, D2, and D3 sites are located in slightly different off-centered positions in nonidentical, distorted Ca₄ interstices.

To further probe the nature of the deuterium bonding in CaSiD₁₊, we have studied the deuterium vibrations in both phases. Figure 4 shows the vibrational spectra for CaSiD₁₊ measured at 3.5 K. The vibrational peak evident near 63.4 meV for CaSiD₁₂ is largely absent for CaSiD, matching the disappearance of the (101) diffraction peaks in the corresponding CaSiD pattern. Therefore, this peak can be directly associated with the D4 atoms in the Ca₃Si sites. In addition, the CaSiD₁₂ spectrum does not reveal any distinct one-phonon peaks associated with stretching modes of the predicted Si-D covalent bond, which would be expected below 180 meV based on the 180–190 meV stretching energies for Si-D bond lengths near 1.48 Å. This result, however, is obscured somewhat by the broad multiphonon band present in our spectrum combined with the realization that only one-sixth of the total D atoms reside in Ca₃Si sites, meaning that only less than 6% of the integrated phonon intensity is expected to be due to the Si-D stretching modes.

It should be noted that analogous NVS measurements for CaSiH₁₊ (not shown here) produced similar vibrational spectra with H vibrational energies roughly a factor of √2 larger than the corresponding D vibration energies for CaSiD₁₊. It is clear that the H and D vibrational spectra exhibit similar complex bands comprised of multiple overlapping peaks, which indicates that they possess the same structures and experience similar structural variations with changing H(D) concentration.

The NV spectrum of CaSiD is well-reproduced (Fig. 4) using first-principles phonon calculations (similar to the formalism of Ohba et al. within the plane-wave implementation of the generalized gradient approximation to density functional theory (DFT) in the PWSCF package. We used a Vanderbilt-type ultrasoft potential with Perdew-Burke-Ernzerhof exchange correlation. A cutoff energy of 408 eV was used and the full dynamical matrix was obtained from a total of 54 symmetry-independent atomic displacements (0.01 Å). The CaSiD NV spectra were computed for a 10×10×10 q-point grid within the incoherent approximation with instrumental resolution taken into account. More detailed calculations will be presented in a subsequent paper.

Since CaSiD₁₂ possesses partial occupancy of the D4 site, NVS calculations were carried out on structure models with full D4 occupancy, i.e., CaSiD₁³ (same symmetry as CaSiD₁₂ but with 1 D atom/Ca₃Si site) as well as half D4 occupancy, i.e., CaSiD₁₁ (0.5 D atoms/Ca₃Si site with b-axis-directed D4 chains comprised of alternating D atoms and vacancies) using the same procedures and methods. Although the latter configuration decreases the overall symme-

![FIG. 4. (Color online) Neutron vibrational spectra of CaSiD₁₂ and CaSiD. Full width half maximum instrumental resolutions are depicted by the horizontal bars beneath the spectra. Calculated spectra for CaSiD, CaSiD₁₁, and CaSiD₁₁₁₁ delineating both 1 phonon (dotted line) and 1+2 phonon (solid line) contributions are shown with the experimental data. The calculated splitting of D modes in CaSiD₁₁₁₁ and the single mode for CaSiD₁₁ (as discussed in the text) are indicated by arrows.]

try due to the ordering (No. 26, Pmc2₁), it is useful as a basis for calculating the effect of vacancies on the local bonding within CaSiD₁ₓ structures where x<0.33. Starting with the structure model determined from our NPD data, we obtained optimized structures for both stoichiometries very close to the one containing the 1.58 Å Si-H covalent bonds reported by Ohba et al.² It is clear in Fig. 4 that the calculated CaSiD₁₊ vibrational spectra are noticeably dependent on both the occupation and degree of ordering associated with the Ca₃Si (D4) sites. For example, the calculated CaSiD₁₁₁₁ spectrum indicates that full occupation of the D4 sites causes a splitting of the D4-associated vibrational modes parallel to the plane of the Ca₃ triads at 57.3 and 62.6 meV (indicated by arrows in the figure), presumably due to interactions between nearest-neighbor D4 atoms. This splitting disappears (see Fig. 4), yielding a peak near 60.2 meV for the calculated, vacancy-ordered CaSiD₁₁ spectrum, which possesses no such nearest-neighbor pairs. The orthogonal Si-D stretching modes (corresponding to the 1.58 Å bond length) are...
predicted near 142 meV for CaSiD$_{1.33}$ and 147 meV for CaSiD$_{1.17}$.

Compared to calculation, the observed CaSiD$_{1.2}$ spectrum appears to possess a disordered arrangement of occupied D4 sites as reflected by the significantly broadened D4-related vibrational mode centered near 63.4 meV. Aware that the calculated CaSiD$_{1.33}$ and CaSiD$_{1.17}$ NV spectra are not exactly comparable to that of disordered CaSiD$_{1.2}$, there are, nonetheless, notable discrepancies in the 50–70 meV region (e.g., lower predicted peak energies) associated with the Ca$_3$Si-occupied D atoms as well as in the 70–100 meV region mainly associated with the Ca$_4$-occupied D atoms. Of particular note is the higher-than-predicted stretching modes for CaSiD$_{1.2}$ cannot be definitively determined by the present NVS results due to the multiphonon band.

IV. CONCLUSIONS

In conclusion, for the CaSiD structure, neutron scattering results and DFT calculations are in good agreement both in terms of structure and dynamics (i.e., the phonon spectrum). However, this is not the case when additional D atoms are added to the structure in the vicinity of the Si atom. The strong disagreement concerning the location and bonding of D atoms in the Ca$_3$Si interstices raises important questions about the “covalent nature” of the Si-H bonding first suggested in Ref. 2 and also predicted by our own DFT calculations. It is clear that further studies, both experimental and theoretical, are needed to fully understand the structure of the Si-H bonding in this interesting CaSi-hydride phase. A fundamental understanding of the Si-H bonding in the various silicide-based hydrides is critical for the successful theory-driven development of improved hydrogen-storage materials containing Si.

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8Corresponding author. Electronic address: huiwu@nist.gov
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