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Vibrational dynamics of hydrogen and deuterium in crystalline Pd_9Si_2

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Abstract

Crystalline Pd_9Si_2 possesses an orthorhombic structure (*Pnma*) that is characterized by augmented triangular prismatic coordination of the silicon atoms such as that which occurs in several metal-rich transition-metal silicides. Recent neutron diffraction results for deuterium solution in this crystalline phase have indicated that deuterium occupies only one type of interstice, i.e., a Pd-defined pyramidal site in a four-fold position situated on a quadrilateral face of an empty triangular prism. The vibrational dynamics of both H and D located at this site were investigated by neutron vibrational spectroscopy. The low-temperature density of states (DOS) of H in $Pd_9Si_2H_{0.25}$ indicates three well-defined optic vibrations located at 49.4, 67.2 and 75.5 meV. The lowest-energy feature is assigned to the normal-mode vibration perpendicular to the pyramidal base and the two higher-energy features are assigned to the two orthogonal normal-mode vibrations parallel to this base. The low-temperature DOS of D in $Pd_9Si_2D_{0.25}$ indicates corresponding normal-mode energies at 31.4, 50.8 and 57.2 meV. This yields H/D energy ratios of 1.57 for the low-energy and 1.32 for both higher-energy modes, reflecting an unusual potential for this pyramidal site. The room temperature DOS of H in $Pd_9Si_2H_{0.25}$ displays a substantial smearing of the vibrational features, suggesting the presence of significant H diffusional motion at this temperature. Preliminary quasielastic neutron scattering measurements have corroborated this interpretation.

Keywords: Hydrogen; Palladium; Silicon; Vibrations; Neutron scattering

1. Introduction

Pd_9Si_2 can exist as a well-defined crystalline phase that forms peritectically at 1096 K [1] with an orthorhombic structure (*Pnma*) [2] characterized by augmented triangular prismatic coordination of the silicon atoms such as that which occurs in several metal-rich transition-metal silicides, e.g., Co_2Si [3]. Isotherms for H_2 and $D_2(g)$ solution in crystalline Pd_9Si_2 [4] confirm significant solubilities even at room temperature and 0.1 MPa, with measured stoichiometries approaching $Pd_9Si_2H_{0.8}$ at 235 K and 1.2 MPa H_2. Recent neutron diffraction results for $Pd_9Si_2D_{0.22}$ [5] show that deuterium occupies only one type of interstice, i.e., a Pd-defined pyramidal site in a four-fold position situated on a quadrilateral face of an empty triangular prism (see Fig. 1). At room temperature, the dissolved D atoms have five Pd neighbors at distances between 1.74(8) and 2.09(8) Å, and the nearest Si atom is at a distance of 3.02 Å. (N.B., a similar pyramidal site, with two Si atoms at distances of 2.9 and 3.1 Å and involving one of the remaining two quadrilateral faces of the empty triangular prism in Fig. 1, was found to be empty.) The full occupation of the favored pyramidal interstices would yield the stoichiometry Pd_9Si_2D. The distances between these interstices are greater than 3.5 Å

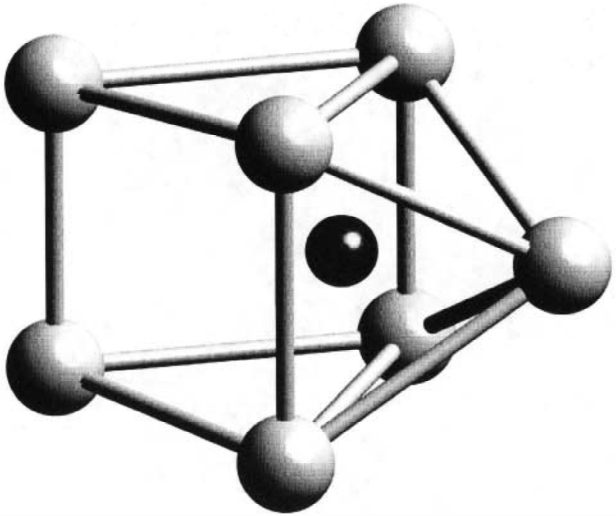

Fig. 1. The interstitial pyramidal site for D (black atom) in solution with Pd_9Si_2, defined entirely by Pd (gray atoms).

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apart, minimizing any significant interactions between the dissolved H(D) atoms.

Deuterium occupation of pyramidal sites has also been found in some Pd–P phases [6–8], although in these phases, additional types of sites are occupied simultaneously. Pyramidal (as well as tetrahedral) coordination of interstitial H in ZrCo has also been suggested from neutron vibrational spectroscopy (NVS) measurements [9]. In contrast, only distorted Pd_6 octahedral sites along with a range of tetrahedral sites have been identified as interstitial sites for H in amorphous $Pd_{11.3}Si_2$ by NVS [10]. In the present study, NVS is used to characterize the vibrational dynamics of both H and D in solution with crystalline Pd_9Si_2 and to investigate the details of the bonding potential associated with the unusual pyramidal site.

2. Experimental

Crystalline Pd_9Si_2 was synthesized as discussed elsewhere [2]. Approximately 12 g of finely powdered sample were sealed in an Al tubular cell equipped with a valve. After evacuating the sample at 373 K to remove any residual H or D, the sample was cooled down in either 0.1 MPa H_2 (Matheson[1] Research purity) or 0.7 MPa D_2 (Spectra Gases[1] Research purity) to near room temperature or below as necessary to obtain the samples $Pd_9Si_2H_{0.25}$ and $Pd_9Si_2D_{0.25}$, in agreement with the previous solubility study [4].

The NVS measurements were performed at the Neutron Beam Split-core Reactor (NBSR) at the National Institute of Standards and Technology using the BT-4 spectrometer with the Cu(220) monochromator and either the low-resolution Be or high-resolution Be-graphite–Be filter analyzers (with assumed final energies of 3 and 1.2 meV, respectively). Before and after the monochromator, collimations of 40'–40' were used for the Pd_9Si_2 and $Pd_9Si_2H_{0.25}$ spectra and 60'–40' for the $Pd_9Si_2D_{0.25}$ spectrum. The instrumental resolutions (full widths at half maximum, FWHM) are denoted by horizontal bars beneath the spectra.

3. Results and discussion

The high-resolution, low-temperature, density-of-states (DOS) spectrum of H in $Pd_9Si_2H_{0.25}$ in Fig. 2 indicates three well-defined optic vibrations located at 49.4, 67.2 and 75.5 meV. This is in stark contrast to the broad distribution of vibrational energies (maximized at ~60 meV) that was observed for H dissolved in amorphous $Pd_{11.3}Si_2$ [10]. A simple three-Gaussian fit of the crystalline $Pd_9Si_2H_{0.25}$ spectrum (ignoring the probable minor contributions of multiphonon scattering at energies above the main features) indicates three modes of roughly equal intensity, consistent with the expected sole occupation of the pyramidal site. By symmetry considerations, the lowest-energy feature is assigned to the normal-mode vibration perpendicular to the pyramidal base and the two higher-energy features are assigned to the two orthogonal normal-mode vibrations parallel to this base. The nondegeneracy found for the higher-energy modes reflects the non-square nature of the pyramidal base. For comparison, the relatively featureless Pd_9Si_2 spectrum is also shown. The low-temperature DOS spectrum of D in $Pd_9Si_2D_{0.25}$ at the top of Fig. 2 yields corresponding normal-mode energies at 31.4, 50.8 and 57.2 meV. The somewhat noisier D spectrum reflects the small amount of sample involved and the much smaller incoherent scattering cross section for D compared to H. There are indications of additional scattering features above 60 meV, but it is unclear how much of this is due to vibrational contributions from the low-energy overtone, multiphonon scattering and residual H in the deuterated sample. More definitive results will have to await further experiments using larger samples and higher D as well as H concentrations. Nonetheless, a comparison of the current H and D spectra give H/D energy ratios of 1.57 for the low-energy and 1.32 for both higher-energy modes, reflecting an unusual potential for this pyramidal site.

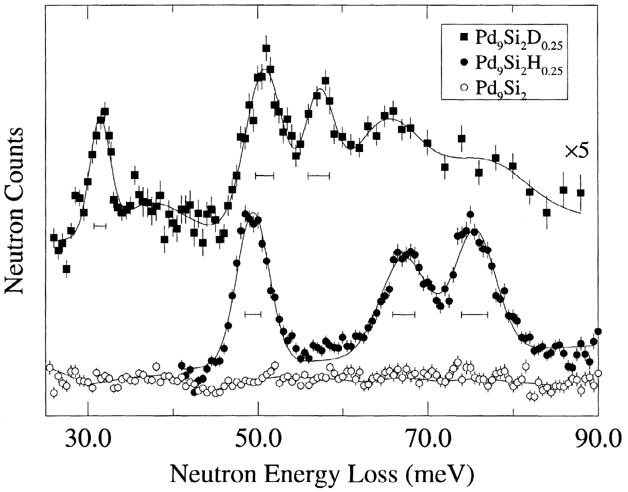

Fig. 2. High-resolution DOS spectra of Pd_9Si_2, $Pd_9Si_2H_{0.25}$ and $Pd_9Si_2D_{0.25}$ at 20 K.

The low-resolution DOS spectra of H in $Pd_9Si_2H_{0.25}$ at 20 and 296 K are compared in Fig. 3. The 20-K spectrum, measured out to 174 meV, illustrates roughly harmonic behavior for the three normal-mode overtones, despite the unusual H/D energy ratios. At room temperature, a substantial smearing of the vibrational features occurs, which would suggest the presence of significant H diffusional motion at this temperature, and/or significant anhar-

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[1] Manufacturers are identified in order to provide complete identification of experimental conditions and such identification is not intended as a recommendation or endorsement by the NIST, nor does it imply that the products are necessarily the best available for the purpose.

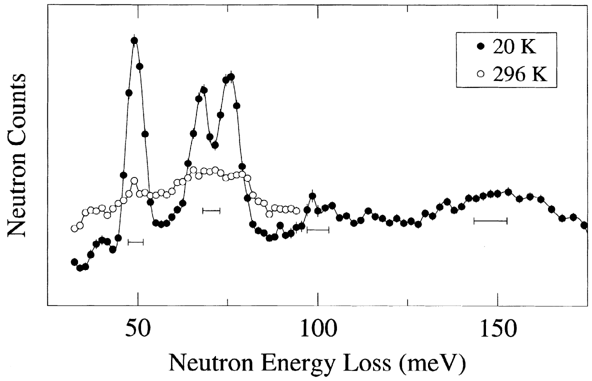

Fig. 3. Low-resolution DOS spectra of $Pd_9Si_2H_{0.25}$ at 20 and 296 K.

monicity. A preliminary quasielastic neutron scattering measurement of this sample at room temperature, using the Fermi-chopper time-of-flight spectrometer at NIST, indicates the clear presence of a Lorentzian quasielastic component due to localized H motion beneath the Gaussian elastic component, which is consistent with the NVS result. Further experiments are underway to characterize the H diffusive motion in this system. This motion may have similarity to the oscillatory type of H short-range diffusion found in $Pd_3P_{0.8}H_{0.2}$ [11] between two crystallographically equivalent, Pd-defined, pyramidal sites. These sites are located near the midpoints of two quadrilateral faces of an empty prism, similar to the normally occupied and empty pyramidal sites in $Pd_9Si_2D_{0.22}$.

4. Conclusions

The optic-vibrational DOS observed for both H and D in $Pd_9Si_2H(D)_{0.25}$ indicate three well-defined, normal-mode vibrations at low temperature, in good agreement with the novel pyramidal interstitial site identified by neutron powder diffraction at a similar D concentration. Confirming site occupancies and vibrational DOS at higher H and D concentrations awaits additional experiments. The different H/D energy ratios for the individual normal-mode vibrations indicate an unusual site potential. Both inelastic and quasielastic neutron scattering data for $Pd_9Si_2H_{0.25}$ suggest the presence of significant H diffusional motion at room temperature and have prompted further neutron scattering investigations in order to identify the nature of the hydrogen motion in more detail.

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