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Total-energy study of hydrogen ordering in PdH_x $(0\leqslant x\leqslant 1)$

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We studied total energies of various ordered structures of PdH_x (in which hydrogen occupies the octahedral sites within the fcc Pd lattice) using the pseudopotential method and a plane-wave basis within the local-density-functional approximation. The structures considered include the (420)-plane ordering of hydrogen atoms at different concentrations. For $x\geqslant\frac{1}{2}$ we found that the NiMo- and Ni_4Mo $(D1_a)$-type structures at $x=\frac{1}{2}$ and $x=\frac{4}{5}$, respectively, were energetically favored phases, in agreement with the superlattice reflections found in previous neutron-scattering measurements. For the intermediate concentrations, linear variation of the formation energy as a function of x in several (420)-ordered structures explained the observed short-range order. In contrast to an earlier proposal, we did not find the Fermi surface imaging effect responsible in this case. The overall energy variation in different phases indicates the importance of going beyond pairwise interactions between interstitial hydrogen atoms in this system.

Metal-hydrogen systems have continuously attracted much attention as prototypes for studying certain basic physical properties and for their technological applications.[1–3] The palladium-hydrogen system is most extensively studied both experimentally and theoretically. When hydrogen goes into fcc palladium, it occupies octahedral interstitial sites within the slightly expanded metal lattice, as determined by neutron-diffraction studies[4] for PdD_x $(x<1)$. Since the number of available octahedral sites is equal to that of metal atoms, the ideal saturation concentration corresponds to $x=1$. At low concentration, one has a solid solution phase with hydrogen randomly occupying the octahedral sites. By measuring a series of equilibrium concentrations as a function of surrounding H_2 (or D_2) pressure at different temperatures, one can construct the temperature-concentration phase diagram. It contains a characteristic spinodal decomposition with regions where two solid solutions (α and α' phases) of different concentrations coexist.[5] One of the special properties of the Pd-H system is the so-called 50-K anomaly found in the high-density α' phase (sometimes also called the β phase) at low temperatures. Researchers observed it in measurements of the specific heat,[6] resistivity,[7] internal friction,[8] and Hall coefficients,[9] for x between 0.6 and 0.8. Depending on the amount of hydrogen in the sample, the anomaly temperature varied in the 50–80 K range. A series of neutron-scattering experiments determined the origin of these anomalies due to structural changes in the deuterium (hydrogen) arrangements. It involves various ordering processes of the interstitially dissolved deuterium (hydrogen) at the octahedral sites,[10] including long-range-ordered structures, as well as a complicated short-range order in certain concentration range.

As for the long-range order, a neutron-scattering experiment by Anderson *et al.*[11] found a weak but sharp superlattice reflection at the (1, 1/2, 0) reciprocal-lattice point superposed on a diffuse background for $x\approx 0.64$, suggesting an interstitial structure with $I4_1/amd$ symmetry. It is stoichiometric at $x=0.5$, consisting of two (420) planes of deuterium atoms followed by two empty ones. At slightly higher concentrations (x = 0.76 and 0.78),[12,13] neutron data found another long-range (420)-plane ordering where superlattice reflections occurred at (4/5, 2/5, 0) and equivalent points. In this case deuterium atoms occupy four (420) planes and leave one empty, forming a Ni_4Mo-type $(D1_a)$ structure. However, at intermediate concentrations, short-range order was present, giving rise to a broad diffuse intensity in the vicinity of (1, 1/2, 0).[13,14] These diffuse intensity distributions existed over the whole concentration range

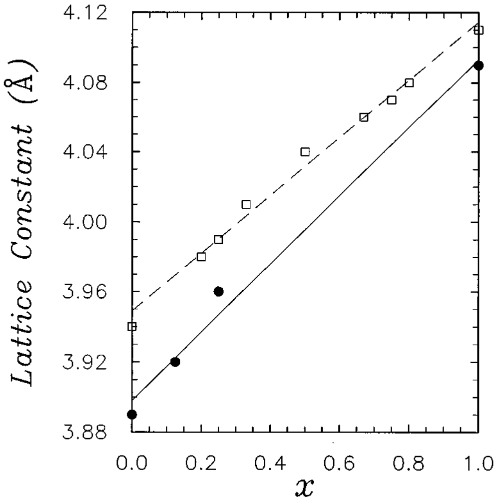

FIG. 1. Calculated equilibrium lattice constants as a function of hydrogen concentration (squares). Measured values are denoted by solid circles. The lines are linear fits.

TABLE I. Symmetry of various ordered phases considered in the calculation and their lattice constants.

	Structure	Symmetry		Lattice constant (Å)
PdH_0	fcc	O_h^5	$Fm3m$	3.94
$PdH_{0.2}$	$D1_a$ (Ni_4Mo)	C_{4h}^5	$I4/m$	3.98
$PdH_{0.25}$	$L1_2$	O_h^1	$Pm3m$	3.99
	$D0_{22}$ (Ni_3Mo)	D_{4h}^{17}	$I4/mmm$	3.99
$PdH_{0.33}$	Ni_2Mo	D_{2h}^{25}	$Immm$	4.01
$PdH_{0.50}$	$L1_0$	D_{4h}^1	$P4/mmm$	4.04
	NiMo	D_{4h}^{19}	$I4_1/amd$	4.04
$PdH_{0.66}$	Ni_2Mo	D_{2h}^{25}	$Immm$	4.06
$PdH_{0.75}$	$D0_{22}$ (Ni_3Mo)	D_{4h}^{17}	$I4/mmm$	4.07
	$L1_2$	O_h^1	$Pm3m$	4.07
$PdH_{0.80}$	$D1_a$ (Ni_4Mo)	C_{4h}^5	$I4/m$	4.08
PdH_1	fcc	O_h^5	$Fm3m$	4.11

$0.64<x<0.78$, which were quite complicated and concentration dependent. Blaschko *et al.*[13,14] described the short-range-ordered state in terms of mixed microdomains consisting of cells of the Ni_nMo type, which have similar structures but different sequences of (420) planes occupied by interstitial deuterium. By locally exchanging one or two occupied and empty sites, one can transform these unit cells into each other. The observed intensity distribution can be described as an ensemble average of unit cells of these structures fitting together like mosaic tiles.

Researchers often use a three-dimensional lattice gas to model hydrogen ordering in metals. In this model each interstitial site is either occupied or empty, and so it is equivalent to an Ising system with spin 1/2. Previous lattice-gas studies of hydrogen ordering in palladium employed only two-body interactions,[15,16] which could not account for all observed phases. Therefore, first-principles calculations of phase stability of different ordered structures will be extremely useful to clarify experimental observations and to provide the binding parameters. For the palladium-hydrogen system, first-principles calculations have been applied to studying hydrogen vibrational frequencies,[17,18] electronic structures of PdH and Pd_4H,[19–21] and binding within pairs of hydrogen in the octahedral cage.[22] In the present paper, we focus on a different aspect, the energetics of PdH_x and H ordering. We have investigated an extended collection of ordered phases, including a series of (420)-plane-ordered structures, and examined their relative stability. From the calculated energy spectrum, we will discuss both the long- and short-range orderings.

Our calculations used the *ab initio* pseudopotential density-functional approach within the local-density approximation.[23] We employed the Born-Oppenheimer approximation within which the electronic properties for PdH_x and PdD_x are identical. Using a soft pseudopotential,[24] we expanded the wave functions in plane waves for both palladium and hydrogen. We generated the palladium pseudopotential from its ground-state atomic configuration $4d^{10}5s^05p^0$ with core-radius cutoffs of 2.7, 2.8, and 2.2 a.u. for the s, p, and d components, respectively, and the hydrogen s pseudopotential with a radial cutoff of 0.88 a.u. The s potential was chosen as the local potential. An energy cutoff of 60 Ry gave a good convergence, which corresponded to about 900 plane waves per atom. For the full fcc symmetry, we used 28 k points in the irreducible Brillouin zone (corresponding to 864 distinct reducible vectors in the full zone). This number varies in other supercell calculations. We used the Gaussian smearing method[25] with a width of 0.1 eV to accelerate the convergence of the total energy (<0.1 mRy) with respect to the number of k points. The Hedin-Lundqvist exchange-correlation formula[26] was used. At self-consistency, the total energy is stable to within 10^{-5} Ry per cell. We determined the equilibrium total energy and lattice constant for a given structure by a least-squares fit of the calculated volume-dependent total energy to Murnaghan's equation of state.[27]

We first examined the structural properties of elemental palladium in the fcc structure. The calculated equilibrium lattice constant, cohesive energy, and bulk modulus were within 1.2%, 1.0%, and 6.0% of experimental values,[28] respectively. These results were consistent with a previous pseudopotential mixed-basis calculation.[21] For PdH with H filling up all octahedral sites, the lattice constant expanded by 4.2% to 4.11 Å (see Fig. 1), which is within 1% of the observed value.[29] For ordered phases of PdH_x with $0<x<1$, one needs bigger unit cells with largely reduced symmetry and an increased number of plane waves. We investigated seven intermediate hydrogen concentrations at $x = 1/5$, 1/4, 1/3, 1/2, 2/3, 3/4, and 4/5. These included six different hydrogen-ordering configurations: $D1_a$ (Ni_4Mo-type), $D0_{22}$ (Ni_3Mo-type), Ni_2Mo-type, $L1_2$, $L1_0$, and "40" (NiMo-type),[30] which will be described below.

The $L1_2$ structure at $x = 1/4$ and $x = 3/4$ and the $L1_0$ structure at $x = 1/2$ all have a fcc cubic unit cell containing four palladium atoms. Four octahedral sites exist in this cubic cell. Adding a hydrogen at one of these octahedral sites gives Pd_4H_1 ($PdH_{0.25}$ in the $L1_2$ structure). Filling one more hydrogen atom into another octahedral site produces Pd_4H_2 ($PdH_{0.50}$ in the $L1_0$ structure). Occupying three out of four octahedral sites yields Pd_4H_3 ($PdH_{0.75}$ in the $L1_2$ structure).

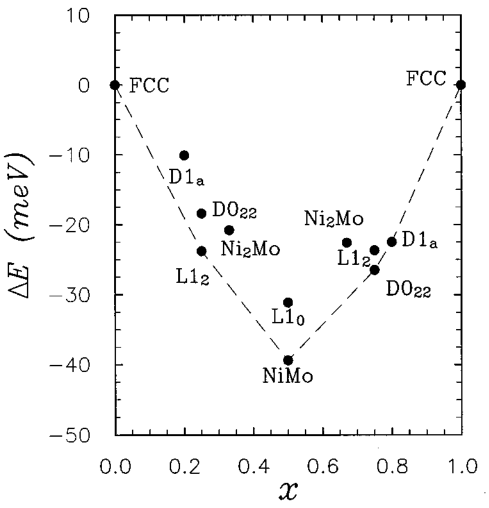

FIG. 2. Formation energies defined in Eq. (1) for structures listed in Table I. The dashed line represents the lowest-energy states.

The space group for both Pd_4H_1 and Pd_4H_3 is O_h^1 (or $Pm3m$). The structure of Pd_4H_2, however, possesses a lower symmetry with the space group being D_{4h}^1 (or $P4/mmm$). Thus the number of symmetry operations is reduced from 48 in O_h^1 to 16 in D_{4h}^1. This unit cell is 4 times larger than the rhombohedral primitive cell of the fcc crystal, and the number of plane waves is accordingly increased to about 3600.

We also considered (420)-plane-ordered structures. At $x = 4/5$ four (420) planes are filled by H followed by one plane of vacant interstitial sites. It corresponds to a $D1_a$ (Ni_4Mo-type) structure with a space group C_{4h}^5 (or $I4/m$). Similarly, for $x = 3/4$ three (420) planes are filled by H followed by a vacant one. It corresponds to a $D0_{22}$ (Ni_3Mo-type) structure with a space group D_{4h}^{17} (or $I4/mmm$). One can construct the Ni_2Mo-type structures at $x = 1/3$ (2/3) similarly by filling (vacating) one of every three planes. The NiMo-type structure ($x = 1/2$) consists of two (420) planes occupied by H atoms followed by two empty ones. Table I gives a summary of symmetry.

We evaluated total energies as a function of lattice constant for all ordered structures described above and found the equilibrium lattice constant as a function of x. As shown in Fig. 1, they compared well with measurements, with a difference of about 1%. To examine the relative stability of various phases, we consider the following formation energy ($T=0$) for configuration σ with concentration x:

$$\Delta E(\sigma,x)=E(\sigma,x)-xE(\mathrm{PdH})-(1-x)E(\mathrm{Pd}). \qquad (1)$$

These formation energies are shown in Fig. 2, with stable structures connected by dashed lines. At $x = 1/2$, the NiMo-type arrangement definitely has a lower formation energy than the other structure $L1_0$, favoring a (420)-plane ordering. The other two stable (420)-ordered structures are $D0_{22}$ (Ni_3Mo-type) at $x = 3/4$ and $D1_a$ (Ni_4Mo-type) at $x = 4/5$. These three phases are almost on a straight line in Fig. 2. Taking into account the computational uncertainty that is of the order of a few meV, we cannot further separate them from this linear variation. This means that for a given concentration between $x = 0.5$ and 0.8, combinations of these phases will have similar energies. Note that another (420)-ordered phase, Ni_2Mo (with a stoichiometic concentration of $x = 2/3$), is slightly above this line in Fig. 2. It is, therefore, less likely to stablize this phase. In fact, the neutron data for $x=0.64$ at low temperatures found a long-range order of the NiMo type ($I4_1/amd$ symmetry), not the Ni_2Mo type.[11] Between $x=0.65$ and 0.70, the observed short-range order from the diffuse scattering contours centered around the (1, 1/2, 0) point at 40 K can be explained by mixed microdomains of the NiMo and Ni_3Mo ($D0_{22}$) types.[14] The current total-energy results support this description. Further concentration and temperature increases will favor the occurrence of Ni_4Mo ($D1_a$) and Ni_2Mo microdomains, respectively. A long-range order of the Ni_4Mo type ($D1_a$) will appear when the concentration gets high enough. These are all consistent with neutron-scattering data.[13,14]

Within the lattice gas model with only two-body interactions, ordering occurs if the Fourier transform of the interaction, $V(\vec{k})$, exhibits extremes at "special points" in the reciprocal space. This picture could not explain the occurrence of diffuse intensity maximum in the neutron data near but outside the (1, 1/2, 0) point at high temperatures for the concentration range $0.71<x<0.78$. Blaschko[31] proposed that this distribution is related to secondary minima in $V(\vec{k})$ at wave vectors connecting flat portions of the Fermi surface. The arguments were based on a rigid-band approximation given the band structure of PdH, where the Fermi surface is convex in the ΓK direction. Decreasing hydrogen concentration lowers the Fermi level, and at a certain point the Fermi surface may go flat, with the $2k_F$ vector pointing to the vicinity of the (1, 1/2, 0) point. We checked the self-consistent electronic structures of (420)-plane-ordered phases in this concentration range ($x = 2/3$, 3/4, and 4/5), but did not find flat Fermi surfaces in the corresponding direction. We feel that higher-order interactions may be quite important in this case. Two-body interactions alone are insufficient to describe the energy distribution of various phases shown in Fig. 2.

Another unusual feature in Fig. 2 is that the $L1_2$ structure is slightly lower in energy than the $D0_{22}$ structure at $x=1/4$. Should a low-temperature ordered phase exist in this concentration range, it is likely to be the former. This is different from what octahedral hydrogen exhibits in other fcc lattices, for example, the superstoichiometric dihydrides of rare-earth metals, MH_{2+x}. In those cases, the $D0_{22}$ ordering is found energetically favorable in calculations[32] and observed experimentally.[33] However, those are quite different systems, in which hydrogen fills tetrahedral sites before occupying the octahedral sites.

In summary, we examined the energetics and H ordering in the PdH_x system by pseudopotential total-energy calculations. The study covers an extended hydrogen concentration range and explores a variety of ordered structures. We found that for PdH_x ($x\geqslant 1/2$) the system favors the (420)-plane ordering, which is consistent with superlattice reflections observed in neutron measurements. We also found a degeneracy in energy for the concentration range of $0.6<x<0.8$, but were not able to connect it with the Fermi surface imaging effect.

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