RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 40, NUMBER 3 15 JULY 1989-II

Multiple deuterium occupancy of vacancies in Pd and related metals

P. Nordlander
Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08855-0849

J. K. Nørskov
Laboratory of Applied Physics, Technical University of Denmark, DK-2800 Lyngby, Denmark

F. Besenbacher
Institute of Physics, University of Aarhus, DK-8000 Aarhus C, Denmark

S. M. Myers
Sandia National Laboratories, Albuquerque, New Mexico 87185
(Received 18 April 1989)

The binding energies of up to six deuterium atoms into monovacancies of Pd, Ni, Fe, Cu, Nb, and Mo have been calculated using the effective-medium theory. For all metals it is found that at least six D atoms can be accommodated in the vacancy. Of the systems studied the deuterium-deuterium interaction is found to be least repulsive for Pd. This multiple occupancy of the vacancy defect can have potentially significant implications for the recently proposed fusion of D atoms in Pd.

Recent discussions[1,2] concerning the possibility of room-temperature fusion of D atoms in certain transition metals such as Pd open up questions relating to the influence of vacancies on the D behavior in transition metals. Metal vacancies would be created by the energetic charged particles and neutrons generated in fusion events; such defects can remove substantial numbers of D atoms from interstitial solution, and they may provide sites for nucleation of dense D plasmas.

In several previous papers we have applied the effective-medium theory to the calculation of heats of solution and vacancy trapping energies of hydrogen and deuterium in transition metals.[3-6] The purpose of the present paper is to extend this treatment to Pd and some other transition metals that could be of potential interest in the context of room-temperature fusion and hydrogen storage. We also compare the theoretical calculations with new experimental data. The method of calculation has been reported elsewhere[5,6] and will be reviewed only briefly here. We will present results for Pd, Nb, Mo, and Cu together with the old Ni and Fe results and present a discussion of the physical factors that influence the energetics of multiple D occupancy in metal monovacancies.

In the effective-medium theory,[7,8] the total energy of N deuterium atoms in a metal vacancy can be written as a sum over the involved deuterium atoms

$$E(\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_N)=\sum_{k=1}^{N}[\Delta E^{\rm eff}_{\rm hom}(\bar{n}^{\rm tot}(\mathbf{R}_k))+\Delta E^{\rm hyb}(\mathbf{R}_k)+\Delta E^{\rm ps}(\mathbf{R}_k)]\,, \quad (1)$$

where ps represents pseudopotential. $\bar{n}^{\rm tot}(\mathbf{R}_k)$ is the average electron density in the neighborhood of deuterium atom k, and can be estimated by linear superposition of atomic electron densities:

$$\bar{n}^{\rm tot}(\mathbf{r})=\bar{n}^{\rm substr}(\mathbf{r})+\sum_{j\neq k}\Delta\bar{n}(\mathbf{r},\mathbf{R}_j)\,, \quad (2)$$

where $\bar{n}^{\rm substr}(\mathbf{r})$ is the average metal electron density at position $\mathbf{r}$ in the vacancy, and $\Delta\bar{n}(\mathbf{r},\mathbf{R}_j)$ is the electron density at position $\mathbf{r}$ induced by the deuterium at position $\mathbf{R}_j$. For the low D occupancies considered in the present application, the relaxation of the metal atoms can be neglected, and the total energy E is a function of the $3N$ coordinates of the D atoms.

The equilibrium configuration of the D in the vacancy is obtained by a multidimensional minimization of the D coordinates. This process is computationally tedious and at present we have only treated up to six D atoms. The minimization is performed as follows: First a certain configuration of the D's is guessed. Then the energy of the D systems is minimized by symmetrically varying the binding distance to the nearest metal atom (100) plane. After this initial minimization a steepest descent method is used to move each D to the nearest local minimum. This part of the minimization displaces the D somewhat out of the symmetrical position. The search for the energy minimum is repeated until a local minimum is obtained. The zero-point energy of deuterium atom k is then estimated by calculating the curvature of E as function of $\mathbf{R}_k$ and the procedure is repeated for several initial configurations. The equilibrium configuration $E(N)$ is chosen as the lowest energy of the calculated local minima.

Before presenting the results, we will review some general features of hydrogen interactions with solids. The dominant contribution to the binding energy of a single D to a metal [$N=1$ in Eq. (1)] comes from the $\Delta E^{\rm eff}_{\rm hom}$ term. This term represents the interaction between D and the metal valence electrons and only depends on the average electron density around the D. There exists an optimal density $\bar{n}_0$ for which this term is at minimum. On a metal surface or in an open-volume defect inside a metal, the D is relatively free to move to a position close to this density. The binding energy of deuterium to such positions is

 © 1989 The American Physical Society

TABLE I. Calculated vacancy trapping energies $\Delta E(N)$ [Eq. (3)] as a function of occupancy. We also show the experimentally obtained values for N = 1, $\Delta E^{\text{expt}}(1)$ (Refs. 5, 6 and 9–11). The energies are in eV.

Metal	$\Delta E^{\text{expt}}(1)$	$\Delta E(1)$	$\Delta E(2)$	$\Delta E(3)$	$\Delta E(4)$	$\Delta E(5)$	$\Delta E(6)$
Ni	0.44	0.52	0.48	0.19	0.24	0.17	0.27
Cu	0.42	0.30	0.29	0.18	0.18	0.11	0.18
Fe	0.63	0.83	0.79	0.54	0.51	0.41	0.42
Mo	1.03	0.96	0.95	0.80	0.73	0.71	0.70
Pd	0.23	0.26	0.27	0.28	0.28	0.29	0.30
Nb		0.59	0.56	0.61	0.53	0.52	0.55

therefore large. In an interstitial position the electron density is, in general, much higher than this optimal density, so the binding energy will be much smaller. It is this energy difference that makes it energetically favorable for the D to accumulate in vacancies. The ΔE^{hyb} and ΔE^{ps} terms in Eq. (1) represent the hybridization between the D and the d electrons in the metal and the interactions between the D and the metal atom cores. At the typical D metal atom distances that appear in vacancies these terms are attractive and displace the D atoms into positions of slightly higher density than $\bar{n}_0$.

The result of the calculation is summarized in Table I, and Fig. 1, where the calculated vacancy trapping energies,

$$\Delta E(N) = E(N) - E(N-1) - E^{\text{int}}, \tag{3}$$

are shown together with the experimentally determined values[5,6,9–11] as functions of N for Pd, Nb, Cu, Mo, Ni, and Fe. The interstitial binding energies E^{int} have been calculated earlier,[3] using the same method as in the present paper. We first note that for all metals considered, it will be energetically favorable for up to six D atoms to accumulate in the vacancy. Even for the highest occupancies, the binding energy in the vacancy is lower than at the interstitial site by a few tenths of an eV. We also note that the absolute agreement (see Table I) between the calculated energies and those obtained experimentally is very good.

From Fig. 1 it can be seen that the binding energy of D changes with occupancy of the vacancy. The reason is the deuterium-deuterium interactions. When several D atoms occupy the vacancy, the distances between the D atoms become relatively small and such interactions can be significant. The calculated D-D interaction is weakly attractive for Pd, weakly repulsive for Nb, and strongly repulsive for Cu, Mo, Ni, and Fe. These findings are in good quantitative agreement with the experimental findings of a rather strong D-D repulsion in Cu, Mo, Ni, and Fe vacancies and a much weaker interaction in Pd vacancies.

The D-D interaction is mediated through the $\Delta\bar{n}(\mathbf{r},\mathbf{R}_j)$ term. This term describes the electron density induced by a D embedded into a metallic host.[12] For small $|\mathbf{r}-\mathbf{R}_j|$ this term is positive. This is due to the formation of a screened D. At larger separations $\Delta n(\bar{r},\bar{R}_j)$ is negative, reflecting the depletion of electron charge density associated with the formation of the screened D. At still larger separations this term exhibits Friedel oscillations.

The general features of the results in Fig. 1 can be understood directly from the geometry of the problem. A monovacancy in a fcc or bcc lattice is surrounded by six (100)-type lattice planes that each contain four nearest-neighbor metal atoms. We will refer to these planes as the sides of the vacancy.

In Table II, we list how the bond length between the D atoms and the nearest-neighbor metal atoms, as well as the minimum distance between the D atoms, varies with occupancy. The data refers to the results obtained from the initial symmetrical minimization.

Pd has a rather large lattice constant, and the D bind to a position very close to the side of the vacancy ($z = 1.2$

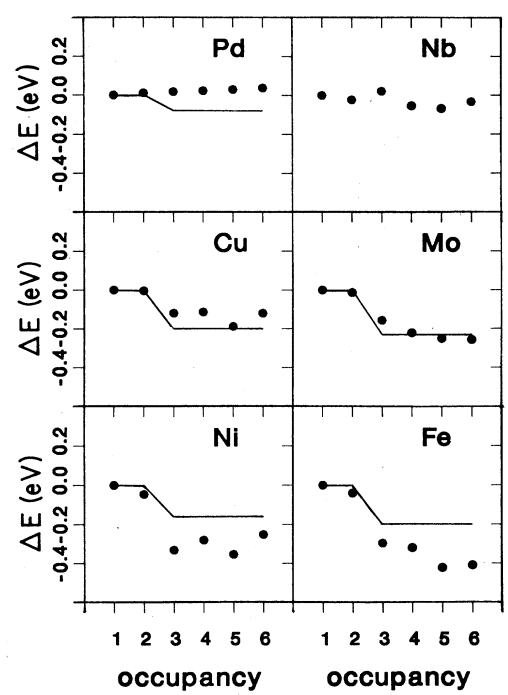

FIG. 1. Calculated trapping energy [Eq. (3)] of deuterium as function of D occupancy in monovacancies in Pd, Ni, Mo, Cu, Nb, and Fe. The solid lines are the experimental data (Ni, Ref. 5; Fe, Ref. 6; Cu, Ref. 9; Mo, Ref. 10; Pd, Ref. 11). The energy units are in eV and the energies are shown relative to the trapping energy of the first D.

TABLE II. Calculated deuterium-metal atom distance d(D-M), distance from the side of the vacancy z, and deuterium-deuterium distance d(D-D) as function of occupancy in a monovacancy. All units are in bohr.

Metal	Occupancy	d(D-M)	z	d(D-D)
Fe	1	4.10	1.44	
	2	4.02	1.22	2.99
	3	3.90	0.72	2.81
	4	3.89	0.66	2.89
	5	3.88	0.55	3.05
	6	3.87	0.55	3.05
Mo	1	4.43	1.40	
	2	4.45	1.46	3.03
	3	4.31	0.91	2.92
	4	4.30	0.85	3.01
	5	4.27	0.73	3.18
	6	4.27	0.73	3.18
Ni	1	3.86	1.97	
	2	3.80	1.83	2.98
	3	3.57	1.29	2.87
	4	3.54	1.22	2.97
	5	3.50	1.09	3.16
	6	3.48	1.02	3.26
Pd	1	3.87	1.21	
	2	3.87	1.21	4.94
	3	3.87	1.20	3.51
	4	3.87	1.20	3.51
	5	3.86	1.19	3.50
	6	3.86	1.19	3.50

a.u.) As the D occupancy is increased the new D atoms can bind to the other sides of the vacancy. The D-D separations are thus rather large. At such distances the D induced electron densities $\Delta\bar{n}$ are negative, causing a depletion of the electron density in the vacancy. This reduction of electron density slightly increases the contribution of the $\Delta E_{\rm hom}^{\rm eff}$ term to the total energy. For Fe, Mo, and Ni the lattice constant is smaller and the D binds relatively far from the side of the vacancy. As the occupancy is increased the D-D distances will thus be rather small and each deuterium atom will feel a positive electron density from the other D atoms. This will cause the D to relax away from each other. This relaxation costs energy and makes the binding energy smaller. Nb is a rather open lattice and the deuterium-deuterium repulsion is small for occupancies up to $N=6$. We note that the D-D distances obtained within the vacancies in the present case are significantly larger than the nuclear separation in the D_2 molecule (1.4 a.u.), but significantly smaller than in octahedral site solution (Pd: 5.2 a.u.; Ni: 4.7 a.u.; Cu: 4.8 a.u.). Fusion within the vacancy is therefore not anticipated on simple grounds for N less than six atoms; higher occupancies probably are needed.

The proper description of D in single vacancies requires a quantum treatment of the D motion.[13] In the present work the quantum aspects have been approximated by adding the zero-point motion as calculated using a harmonic approximation to the total energy. The calculated multiple binding energies are therefore slightly uncertain. We estimate the errors introduced by this approximation to be smaller than 50 meV.

In conclusion, we have shown that open defects such as vacancies in metals are able to trap a large number of deuterium atoms creating a uniquely high local concentration of D atoms. The occupancies up to six atoms per vacancy studied here represent a lower bound and we cannot exclude even higher concentrations. We have shown that of the metals studied, only in Pd is multiple occupancy favored over single occupancy. Furthermore, although the D-D spacing within the Pd vacancy is still larger than what is believed necessary for fusion, the D-D spacings in the vacancy are nonetheless substantially smaller than in octahedral site solution (5.2 a.u.). This fact may be of importance for the understanding of the proposed room-temperature fusion events in solid Pd. The computational approach developed in the present paper also provides a reliable basis for treating D-D interactions for interstitial solution as well as in other types of defects. Further calculations studying the effects of a localization of many D atoms in a small volume on the many-body wave function describing the motion of the D atoms and their mutual overlap are in progress.

The authors acknowledge valuable comments from Dr. D. C. Langreth and Dr. D. M. Follstaedt. This work is supported by the National Science Foundation under Grant No. DMR-88-01027.

[1]M. J. Fleischman and S. J. Pons, J. Electroanalyt. Chem. **261**, 301 (1989).

[2]S. E. Jones, E. P. Palmer, J. B. Czirr, D. L. Decker, G. L. Jensen, J. M. Thorne, S. F. Taylor, and J. Rafelski, Nature (London) **338**, 737 (1989).

[3]P. Nordlander, J. L. Nørskov, and F. Besenbacher, J. Phys. F **16**, 1161 (1986).

[4]J. K. Nørskov and F. Besenbacher, J. Less-Common Met. **130**, 475 (1987).

[5]S. M. Myers, P. Nordlander, F. Besenbacher, and J. K. Nørskov, Phys. Rev. B **33**, 854 (1986).

[6]F. Besenbacher, S. M. Myers, P. Nordlander, and J. K. Nørskov, J. Appl. Phys. **61**, 1788 (1987).

[7]J. K. Nørskov, Phys. Rev. B **26**, 2875 (1982).

[8]P. Nordlander, S. Holloway, and J. K. Nørskov, Surf. Sci. **136**, 59 (1984).

[9]F. Besenbacher, B. Bech Nielsen, and S. M. Myers, J. Appl. Phys. **56**, 3384 (1986).

[10]S. M. Myers and F. Besenbacher, J. Appl. Phys. **60**, 3499 (1986).

[11]F. Besenbacher *et al.* (unpublished).

[12]P. Nordlander and S. Holmstrom, Surf. Sci. **159**, 443 (1985).

[13]F. Besenbacher, J. K. Nørskov, M. Puska, and S. Holloway, Phys. Rev. Lett. **55**, 852 (1985).