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COMPUTER SIMULATION OF D ATOMS IN A Pd LATTICE

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Abstract

We calculate the equilibrium configurations of a system of deuterium atoms absorbed in palladium. The interaction potential energy is taken as a sum of pair functionals including non-additive effects, which are crucial for this case. We conclude from our calculations that the most probable configuration for the deuterium in the β -phase of PdD involves at least a partial occupation of the tetrahedral sites of the fcc palladium unit cell.

INTRODUCTION

In order to understand neutron emissions and other anomalous nuclear effects detected in metal lattices loaded with deuterium¹⁻³, we want to calculate equilibrium and non-equilibrium properties of metal-deuterium systems via computer simulations. The computational method we have adopted is that of molecular dynamics to calculate the dynamical properties⁴, and damped molecular dynamics for the energy minimization⁵.

There are several specific features of the deuterium-metal system that are absent when deuterons interact in vacuum: *a*) their motion is greatly constrained because of the presence of the lattice, *b*) their interaction is modified by the electronic environment in the solid, *c*) the lattice acts as an energy and momentum absorber. These effects may also appear in a coherent way⁶ within the crystal. Furthermore, there seems to be evidence that non-equilibrium conditions, such as the system going through a phase transition², or the formation of vacancies, imperfections and cracks⁷ may play an important role in the explanation of these anomalous phenomenon. The main object of this study is to understand which, if any, of these properties are relevant.

In the present work, we shall concentrate on the equilibrium configuration of the Pd-D system. The dynamical and non-equilibrium results will be presented elsewhere.

In the next section we introduce the embedded atom method⁸⁻¹⁰ and the corresponding energy expression for the interactions among all the Pd and D atoms. The third section contains the specific values of the parameters chosen for this study, while the last two sections include specific results and the conclusions we can draw from the present configurational study.

CONFIGURATIONAL ENERGY

The Born-Oppenheimer separation of nuclear and electronic motions in a solid allows us to describe the slower nuclear dynamics in terms of a potential energy which depends only upon the nuclear coordinates. This energy function is obtained averaging the total Hamiltonian of the system over the electronic coordinates. In general, approximating the nuclear potential energy by a sum of pairwise additive terms is not a satisfactory approximation. This is particularly true in the case of hydrogen (and its isotopes) atoms in a metal lattice⁸. The inclusion of three- and many-body terms is cumbersome and produces prohibitive computational efforts in a dynamical calculation. What has proven to be a very effective approximation in this instance is the expression of the configurational energy as a sum of pair functionals, *i.e.* a function of a function of the nuclear coordinates⁹. Given that the quantum character of the motion of the electrons is reflected in the electronic density, it is only natural to express the nuclear potential energy as a sum over all atoms of a function of the background density in the system.

In the embedded-atom method⁸⁻¹⁰, the background electronic charge density is taken as a superposition of the spherically averaged atomic charge densities centered on the other atoms. The explicit form of the function $F_i(\rho)$ of the host density contributing to the energy of atom i is determined empirically, and corrected by a pairwise additive function ϕ_{ij} of the internuclear distances R_{ij} , mainly due to the core-core repulsion. The explicit form of the nuclear potential energy V is given as:

$$V(R_{ij}) = \sum_i F_i(\rho^{(i)}) + \frac{1}{2} \sum_{i \neq j} \phi_{ij}(R_{ij}), \quad (1)$$

where the host density $\rho^{(i)}$ is approximated as:

$$\rho^{(i)} = \sum_j \rho_j^{at}(R_{ij}), \quad (2)$$

in terms of the atomic densities ρ^{at} , calculated quantum mechanically¹¹. The resulting V is then a function of the internuclear distances R_{ij} and involves a double summation over the atoms.

When the function $F_i(\rho)$ is taken to be proportional to the host density, V reduces to a sum of pair potentials. This turns out to be a good approximation for the case of helium absorbed in a lattice⁸. In the case of hydrogen, it has been shown^{8,10} that the approximation defined by Eqs. (1) and (2) can give excellent results if the functions F and ϕ are chosen appropriately. The function $F_i(\rho)$ presents a minimum close to the equilibrium density of the pure stable system of atoms i . For deuterium this is the D_2 molecule, while for Pd this is the fcc configuration of the solid. Furthermore, $F_i(\rho)$ should vanish at the origin and become linear for large values of its argument¹².

PARAMETRIZATION

In order to simulate the motion of the D and Pd atoms, we need explicit expressions for F_{Pd} and F_D as functions of the charge density, as well as the repulsive potentials $\phi(R)$ for the three different pairs, Pd-Pd, D-D, and Pd-D. We have chosen a rational function for $F(\rho)$. The coefficients for Pd were fitted so as to reproduce the correct equilibrium distance and energy of the fcc Pd crystal, as well as the vacancy formation energy:

$$F_{Pd} = \frac{-205\rho + 551\rho^2}{1 + 11.4\rho} \text{ eV.} \quad (3)$$

Distances are measured in \AA , densities in \AA^{-3} , charges in a.u., and energies in eV. The repulsive part has the form of a Yukawa interaction:

$$\phi_{Pd-Pd}(R) = 14.39975 Z_{Pd}^2 \exp(-2\beta_{Pd}R)/R \text{ eV,} \quad (4)$$

where $Z_{Pd} = 46$, $\beta_{Pd} = 1.944 \text{ \AA}^{-1}$. We calculated the charge density for the Pd atom as a spline interpolation of Clementi's¹¹ double- ζ SCF calculation for the $s^2d^8(^3F)$ state.

Cutting off the potential at a distance $R_{co} = 4.669 \text{ \AA}$, we obtain an equilibrium lattice constant $a_0 = 3.891 \text{ \AA}$, a cohesive energy $E_{coh} = 3.910 \text{ eV/atom}$, and a vacancy formation energy $E_{vac} = 1.392 \text{ eV/vac}$. The calculated host density at equilibrium is $\rho_{eq} = 0.04596 \text{ \AA}^{-3}$.

The corresponding expressions for D are:

$$F_D = \frac{-195\rho + 62\rho^2}{1 + 69\rho} \text{ eV,} \quad (5)$$

and

$$\phi_{D-D}(R) = 14.39975 Z_D^2 \exp(-2\beta_D R)/R \text{ eV,} \quad (6)$$

with $Z_D = 1$, $\beta_D = 3.385 \text{ \AA}^{-1}$. With this parametrization we obtain an equilibrium distance $R_{DD} = 0.741 \text{ \AA}$ and a binding energy $E_{DD} = -4.7475 \text{ eV}$ for the D_2 molecule.

Finally, the Pd-D repulsive potential is given by:

$$\phi_{Pd-D}(R) = 14.39975 Z_{Pd}Z_D \exp(-\beta_{Pd-D}R)/R \text{ eV,} \quad (7)$$

with $\beta_{Pd-D} = 4.5 \text{ \AA}^{-1}$. In this way, we obtain a diffusion activation energy of D in Pd of 0.22 eV, in excellent agreement with experiment^{13,14}.

In order to calculate the nuclear trajectories we need to obtain the forces from the potential energy $V(R_{ij})$ as

$$\mathbf{F}_k = -\frac{\partial V}{\partial \mathbf{x}_k}. \quad (8)$$

The particle trajectories are calculated by integrating numerically Newton's equations of motion. We have used Verlet's algorithm⁴ with a time step of 2.5 fs.

The pressure can be calculated from the virial theorem:

$$P = (\sum_k \mathbf{r}_k \cdot \mathbf{F}_k + 2T)/3\Omega \quad (9)$$

where T is the kinetic energy and Ω is the volume.

In order to avoid surface effects, we have used periodic boundary conditions, as is customary in these cases. In all our calculations we have used a periodic length of three or four times the lattice constant a_0 . Since the fcc Pd unit cell contains four Pd atoms, this means a total of 108 or 256 Pd atoms respectively. Both the volume and the total energy are kept fixed during the simulation. This is equivalent to a micro-canonical ensemble calculation.

We have considered several initial positions for the D atoms absorbed in the Pd lattice. The results for the equilibrium configurations are presented below.

RESULTS

As we have already mentioned, the parameters in the potential energy Eqs. (1)-(7) are chosen in such a way as to reproduce *a*) the experimental fcc distance and energy for the Pd crystal, *b*) the energy of formation of a vacancy in the fcc lattice, *c*) the experimental equilibrium distance and binding energy of the D₂ molecule, as well as the overall form of its potential energy curve, and *d*) the migration energy of D in the Pd lattice.

In order to minimize the energy of the D in Pd system, we calculate the classical trajectories in the corresponding force field, damping the energy of the system at each integration time step. Setting to zero all velocity cartesian components having opposite sign to the force component, energy is (artificially) drained, and the system relaxes to the (local) minimum⁵.

There are three symmetric points a D atom can reach: *a*) the octahedral site O , lying midway between second nearest neighbor Pd atoms in the fcc lattice, *b*) the tetrahedral site T , at the center of the tetrahedron formed by four nearest neighbors, and *c*) the midpoint between nearest neighbors S . If all O sites were occupied by D atoms, we would have a PdD composition with the NaCl structure.

Let us start by adding a single D atom to the system of 256 Pd atoms in the basic repeating cube containing 64 unit cells, and look for the equilibrium positions by minimizing the total configurational energy. The D atom will migrate to one of the symmetric sites O , T , or S , depending on its initial position. Taking the parameters given above, the global minimum is given by the D atom in the octahedral position O . The Pd lattice relaxes locally very slightly, giving a minimum distance of 1.944 Å between D and Pd. In the deformed region the Pd-Pd nearest neighbor distance is 2.748 Å (*cf.* 2.751 Å for pure Pd). A D atom in the T position lies higher by 0.08 eV in the corresponding relaxed lattice, while

the S site is 0.40 eV above the global minimum O . There is a saddle point along the line joining the O and T sites. Its energy is 0.22 eV above the O minimum, and it is located a third of the way between T and O . A D atom moving along this line will have to overcome this barrier in order to diffuse from O to T .

Given that we want to understand the required conditions for d-d fusion in this system, we studied different configurations of two D atoms, forced to be in the same unit cell. In this system of 258 atoms, we looked for the equilibrium configurations and found out that there are several possibilities with almost identical energies, but quite different equilibrium D-D distances. A stable state is found to be one with a D_2 molecule centered around the O position, *but* with its axis *tilted* with respect to the central Pd-Pd axis, by an angle of 45° . The D-D distance in this case is 0.923 Å, which compares very favorably with *ab initio* density functional calculations¹⁵, although the more symmetrical configuration studied in Ref. 15 turns out to be a saddle point in our energy surface. Having one of the d nucleus close to the O position and the second one close to the neighboring T position yields the most stable system with an energy 0.055 eV lower, but with a D-D distance of 1.758 Å.

We finally studied the fully deuterated system PdD, showing some peculiarities. The system in this case consisted of 108 Pd atoms and 108 D atoms. In order to find the correct equilibrium state, we allowed the elementary volume to expand. With the potential parameters shown above, the global minimum turns out to show one D atom per octahedral position, as would be expected from the results above. The new lattice constant for this case is $a_0 = 3.94$ Å. A local energy minimum results from having the D atoms in alternating T positions (still 4 D atoms/unit cell), lying 0.07 eV/D atom above the former configuration, *but with a lattice constant* $a_0 = 4.01$ Å, which is much closer to the experimental value for the β -phase of palladium deuteride^{16,17}. Considering this fact, we varied the repulsion Pd-D parameter β_{Pd-D} appearing in Eq. (7). For values between 4.2 and 5.0 Å⁻¹, the relative energy difference between T and O states varied from 0.20 to -0.12 eV. However, the largest lattice constant for the O state was found to be $a_0 = 3.97$ Å, while the corresponding ones for the T state were in the range of 4.01 to 4.10 Å. Whereas using an energy criterion, the choice between having a T or an O equilibrium state is inconclusive, the corresponding values of the lattice constants definitely favor the state in which the D atoms lie on staggered T positions in the β -phase of PdD. This conclusion is similar to the one reached by Mansour, Wolf and Kasowski¹⁸ using an *ab initio* method.

CONCLUSIONS

The equilibrium calculations performed in the Pd-D system indicate that a D_2 "molecule" can be formed around the octahedral position of the fcc palladium lattice at zero temperature. The D-D distance in this calculation turns out to be larger than the free D_2 molecule, but their corresponding electronic host densities

have very similar values. Preliminary dynamical calculations show, however, that at finite temperatures the deuterons do tend to come closer together. Even disregarding non-equilibrium effects, at room temperature our calculations show d-d approximation distances of the order of 0.7 Å as typical. This is due to the high mobility of D in the Pd lattice, as well as to the fact that the two local minima interstitial sites *O* and *T* have very close energies. The constraining action of the lattice will only tend to favor the approximation of the two deuterons.

Our equilibrium calculations of the β -phase of PdD cast some doubt on the orthodox interpretation of finding all D atoms in the octahedral positions¹⁹. They suggest at least a partial occupation of the tetrahedral sites in order to explain the amount of lattice expansion when going from the pure Pd fcc to the PdD crystal. The fact that the lowest state for two D atoms locates one in the *T* position and the second one in the *O* position reinforces this conclusion. This agrees with recent *ab initio* calculations¹⁸, as well as with the interpretation of the anomalous low temperature electrical resistivity and heat capacity of the β -phase given in Ref. 20.

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