Theory of Nickel and Nickel-Hydrogen Complexes in Silicon

R. Jones
Department of Physics, University of Exeter, Exeter EX4 4QL, United Kingdom

S. Öberg
Department of Mathematics, University of Luleå, Luleå S95 187, Sweden

J. Goss
Department of Physics, University of Exeter, Exeter EX4 4QL, United Kingdom

P. R. Briddon
Department of Physics, University of Newcastle-upon-Tyne, Newcastle-upon-Tyne NE1 7RU, United Kingdom

A. Resende
Departamento de Física, Universidade de Aveiro, 3800 Aveiro, Portugal

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Spin-polarized local density functional cluster calculations are carried out on substitutional Ni and Ni-H_2 complexes. We find that Ni^- undergoes a Jahn-Teller distortion along $\langle 100 \rangle$ with Ni moving slightly along the cube axis. The distorted state gives b_1, b_2, and a_1 levels in ascending order of energies within the gap in agreement with experiment. Several candidate NiH_2 defects are investigated: the lowest energy structure consists of a substitutional Ni atom together with two H atoms at antibonding sites to two Si neighbors of Ni. This gives H related vibrational modes and a spin-polarized charge density close to those reported for Pt-H_2.

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The vacancy model of substitutional transition metal (TM) impurities on the far right of the periodic table [1,2] considers that the d levels of the TM impurity lie deep in the valence band of Si and couple weakly with the t_2 levels arising from the T_d symmetry of the ideal vacancy. The important implication is then that the gap levels and structure of the defect are largely determined by those of a perturbed vacancy [3–6]. For Pt^-, Pd^-, and Ni^-, the gap t_2 levels contain three electrons and according to the Jahn-Teller theorem a distortion will occur for an $S = 1/2$ state, leading to a splitting of these levels and a lowering of energy. Deep level transient spectroscopy shows that Ni_s possesses acceptor and donor activation energies at $E_c - 0.45$ and $E_v + 0.16$ eV, respectively [7]. Electron paramagnetic resonance (EPR) measurements on Ni^- [8] and Pt^- [2,9] reveal that the defect has C_{2v} symmetry and, furthermore, uniaxial stress measurements on the EPR lines have shown [9,10] that the gap t_2 levels split into a configuration $b_1^{\uparrow\downarrow} b_2^{\uparrow} a_1^{0}$. This ordering of levels is the reverse to that found for the negatively charged vacancy. Further evidence for the vacancy model has been suggested recently when it was found that Pt-H complexes can be created by high temperature in-diffusion of the impurities [11–14]. Two localized vibrational modes (LVMs) attributed to Si-H have been observed that undergo small shifts in mixed H-D implantation or when the charge state of the defect is changed. These results establish the presence of more than one H in the defect. The first suggestion was that the H atoms bond to two of the four Si atoms surrounding the vacancy. It is the purpose of this work to investigate this model.

As far as we have been aware, there have been no *ab initio* calculations of the Jahn-Teller distortion or the splitting of the t_2 levels, nor of the complexes with H. We report here local density functional spin-polarized calculations on substitutional nickel, Ni_s, and Ni-H_2 complexes using large (up to 133 atoms) H-terminated clusters. A key ingredient is that we allow the atoms surrounding the defect to move, and this enables us to investigate in detail the Jahn-Teller distortion due to Ni_s^- and to obtain the structure and the LVMs of the Ni-H_2 defect. The LVMs are found by two methods. In the first we numerically differentiated the forces on H and the surrounding atoms, and these, together with a previously determined potential, were used to construct the dynamical matrix of the cluster. This gives quasiharmonic LVMs. In the second method [15], the energies corresponding to displacing the H atoms from their equilibrium sites were found and the Schrödinger equation for the oscillator solved numerically using these energies as a potential in accordance with the Born-Oppenheimer approximation. The two methods give rather similar results.

The *ab initio* method has been described previously [16], and it has been adapted for the present study to deal with d orbitals and spin-polarization effects [17,18]. We investigate the case of Ni since spin-orbit coupling is less important in this case than for Pd and Pt. The electronic wave functions of the cluster were expanded in atom-sited

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Gaussian orbitals. Seven independent Gaussian s, p, d orbitals with different exponents were placed on the Ni atom, two on each H atom, and four on the central four Si atoms. The remaining basis consisted of fixed linear combinations of the s and p orbitals with different exponents, and these are centered on the other atoms. The charge density was fitted by a linear combination of s Gaussian functions: 14, 5, and 3 sited on Ni, Si, and H, respectively. Ni and Si pseudopotentials were taken from Ref. [19]. We have shown that the method describes small molecules containing Ni very accurately: The bond lengths of $Ni(CO)_4$, for example, are found to be within 1% of their experimental values. The cluster approach for H defects in bulk Si locates LVMs to within about 100 cm^{-1} [20].

We investigated Ni_s^- embedded in a 71 atom cluster, $NiSi_{34}H_{36}$. The Ni atom was placed along [100] so that the symmetry of the cluster is C_{2v}. Three close-by levels for each spin lay in the gap region, and these are occupied with three electrons according to Fermi statistics corresponding to 0 K; i.e., the lowest was filled, the next filled in the up-spin case only, and the others were empty. The self-consistent energy and forces acting on the central 17 atoms were then found for this $S = 1/2$ configuration, and these atoms were allowed to move to minimize the energy of the cluster using a conjugate gradient algorithm. The Ni atom moved closer to the substitutional site while the surrounding Si atoms moved outwards from their lattice positions. The splitting between the t_2-derived levels gradually decreased, and eventually we were unable to obtain a self-consistent solution. This arises because during the course to self-consistency, the three close-by gap levels, the uppermost of which is empty, cross over, and if, for example, the a_1 state falls below the b_1 state, the charge density and hence potential changes discontinuously. On the next iteration, the level ordering often reverses and the process never converges. This problem of "charge sloshing" is well known and often occurs for close-by levels. It can be overcome by occupying the gap levels with Fermi statistics corresponding to a finite temperature larger than the splitting of the t_2 levels. This spreads out the electrons among the three gap levels and the discontinuity in the charge density arising from crossover is reduced. However, this almost eliminates the Jahn-Teller driving force for the Ni atom to lie off-site. For the finite-temperature calculation the lowest energy configuration corresponded to a structure where the Ni atom is essentially on site, but the four surrounding Si atoms were displaced outwards from their lattice sites by 0.270 Å and two of them were further displaced along [100] by 0.006 Å. Second shell Si atoms were displaced by ≈0.07 Å. The three gap levels were split by only 0.005 eV, and the highest occupied spin-up level was 0.6 eV below the corresponding (but empty) spin-down level. Thus the departure from T_d symmetry is extremely small. The ordering of the t_2-derived gap levels is $b_1^{\uparrow\downarrow} b_2^{\uparrow} a_1^{0}$, the same as that found experimentally.

The problem of obtaining self-consistent solutions can now be overcome by restricting the electronic configuration to be $b_1^{\uparrow\downarrow} b_2^{\uparrow} a_1^{0}$. Then during the passage to self-consistency, there is no discontinuity in the charge density, but the energy levels that are occupied at each stage are not necessarily in ascending order. However, towards the end of the self-consistency cycle the energy levels ordered correctly and the final energy obtained was lower than that obtained by the imposition of a temperature. The Ni atom was then moved along [100] and the equilibrium structure was found to correspond to a displacement of 0.13 Å from the lattice site. The two Si atoms with Cartesian components along [100] were displaced almost radially by (0.15, ±0.25, ±0.22) Å and moved away from each other, whereas the other two Si atoms with components along $[\bar{1}00]$ were displaced (−0.07, ±0.16, ∓0.13) Å so that they approached each other. Curiously, the four Ni-Si bonds are almost identical in length at 2.645 Å. This distortion is similar to that found experimentally for the negatively charged vacancy [21].

Suppose now, we occupy the t_2-derived states according to $a_1^{\uparrow\downarrow} b_1^{\uparrow} b_2^{0}$. This is the configuration found experimentally for the negatively charged vacancy [21] but not for Ni_s^-. Then the self-consistent cluster energy is higher than the previous configuration by 0.017 eV. We note that although we have shown that the C_{2v} distortion has a lower energy than T_d it leaves open the possibility that other symmetries, e.g., D_2 have even lower energies as suggested in Ref. [22]. The slight distortion from T_d to C_{2v} symmetry is consistent with the ease of reorientation of Pt around the central lattice site. This motion occurs for temperatures above 12 K or even when the slightest stress is imposed on the crystal at 2 K [9].

The pseudo wave function of the t_2-derived levels all possess a nodal surface lying between the TM impurity and the surrounding Si atoms and peaks on either side of the Si atoms along $\langle 111 \rangle$. This suggests that H atoms will lie either between Si and Ni in the configuration suggested previously [10,11,13,14], or outside at antibonding (AB) sites as shown in Fig. 1. The effect of H was investigated in a 133 atom negatively charged cluster $NiSi_{70}H_{62}$ where 19 central atoms were relaxed. There were no problems with self-consistency in the present case. For the first defect, the H atoms repelled Ni along [100] from its lattice site by 0.20 Å and formed Si-H bonds of length 1.508 Å with a H-H separation of 1.517 Å. The LVMs due to H were calculated to lie at 2477 and 2511 cm^{-1}. These values are far from the experimental ones for PtH_2 [10–12] and strongly suggest that this model is incorrect. The strong coupling between the H atoms occurs because there is so little room for both Ni and H within the vacancy. The second defect (Fig. 1) when relaxed yielded an energy 0.08 eV below the first structure, the Ni atom moved 0.3 Å along [100] towards the H atoms, and the Si-H lengths became 1.557 Å. The separation between the H atoms was 7.3 Å. The vibrational modes are given in Table I. The

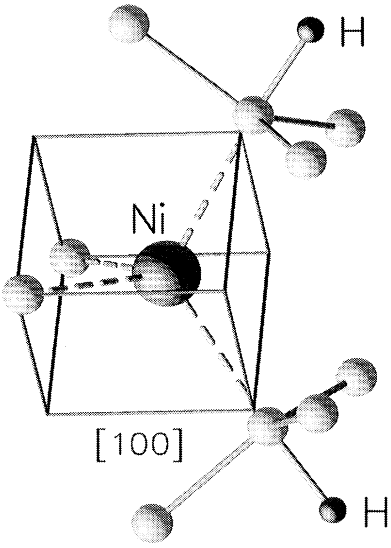

FIG. 1. Ni-H_2 complex with H at antibonding (AB) sites.

two H related modes are slightly split, by 7 cm^{-1}, with the higher mode being A_1. Now, uniaxial stress splitting experiments on PtH_2 [12] show that the upper and lower modes also have A_1 and B_1 symmetries, respectively. The stretch modes are close to those reported for PtH_2 but the bend modes have not yet been detected.

Anharmonic effects are known to be important for H modes [15,23,24], and we investigated their influence in the following way: the two modes at 2009.9 and 2003.2 cm^{-1} represent A_1 and B_1 vibrational modes in which the H atoms move either in phase or out of phase with each other. The energies necessary to displace the H atoms by an amount r, parallel to the Si-H bonds, were evaluated for each of these modes. This energy contains only even powers of r in the B_1 mode, whereas it contains both even and odd powers in the A_1 mode. The Schrödinger equation for the oscillator was solved numerically [15], and the A_1 and B_1 frequencies were then found to be 2037 and 2060 cm^{-1} and are separated by 23 cm^{-1}. However, now the B_1 mode lies *above* the A_1 mode contrary to experiment. Thus even though the separation of the H atoms is very large, 7.3 Å, the two modes are split and their ordering reversed by these anharmonic effects by an amount twice as large as that observed for Pt-H_2. However, there are other anharmonic terms that should be considered. For example, $r_1\theta_1^2 + r_2\theta_2^2$ terms where r_k and θ_k are the changes in the equilibrium Si_k-H_k lengths and angles, respectively. These mix the stretch and bend modes and are only present in the A_1 mode where $r_1 = r_2$. These have the effect of decreasing the mean Si-H length hence pushing up the A_1 frequency. Such a term then might well displace the A_1 mode above that of B_1.

TABLE I. Vibrational modes, cm^{-1}, for the TM H_2^- AB defect.

Calc.	A_1	B_1	A_2	B_2	A_1	B_1
Ni H_2	2009.9	2003.2	903.0	897.2	890.4	889.4
Ni H D	2006.6	1442.5	900.1	889.8	636.6	630.6
Ni D_2	1445.1	1439.9	638.7	634.6	631.6	629.5
Expt.^{a,b}						
Pt H_2	1901.6	1888.2				
Pt HD	1894.6	1366.9				
Pt D_2	1370.7	1362.5				

^{a}Reference [11,12]. ^{b}Reference [27].

We investigated several other models of the defect but all gave energies above that of the AB structure. In addition, their vibrational modes were far from the observed values and often, the B_1 mode lay higher than that of the A_1. We suggest then that the H atoms lie at AB sites in the Pt case especially as its larger size makes it even less likely that H would lie inside.

Further arguments against the configuration in which H atoms are inside the vacancy come from the comparison with LVMs assigned to the vacancy-hydrogen, VH_2, and H_2^* complexes. The former are observed at 2122 and 2144 cm^{-1} [25]. The separation between the H modes here, $\approx$23 cm^{-1}, is larger than that observed in PtH_2 where it might be expected that the TM squeezes the H atoms together, increasing their interaction and the mode splitting. In the case of H_2^*, the AB sited H atom gave an LVM at 1838 cm^{-1} [20] rather close to the stretch mode of the PtH_2 complex, whereas the other H LVM, attributed to H-Si stretch where Si has a tetrahedral environment, has a frequency at 2061.5 cm^{-1}—somewhat higher than that found for Pt-H_2. Recently, Uftring *et al.* [26] analyzed the anisotropic hyperfine parameter in PtH_2 and concluded that the Pt-H distance is about 4.5 Å, which is close to the calculated Ni-H length of 4.28 Å in the AB sited model.

The wave function for the highest occupied level in NiH_2^- (AB) has b_2 symmetry and *vanishes* in the (011) plane containing the two H atoms. This level occurs around midgap in our calculations, and the next lower level is very close to the valence band. The positions of these levels are only approximate, but they suggest that the observed EPR signals are due to PtH_2^- complexes, for it is known that when E_f lies above $E_c - 0.1$ eV, then the defect is not paramagnetic. There must be a second acceptor level corresponding to the filling of $b_2^{\downarrow}$ around $E_c - 0.1$ eV and leading to diamagnetic NiH_2^{--}. Uftring *et al.* [26] also concluded that the defect has two acceptor levels as the effect of illumination on the paramagnetic complex is easily understood to arise from the capture of photogenerated holes by PtH_2^-. In addition, they suggested that the Pt hyperfine data are consistent with the H atoms lying in the nodal plane of the highest occupied level. For NiH_2^-, the contour plots of the pseudo wave functions suggest that the isotropic hyperfine interaction with H would vanish leaving only an anisotropic one. However, spin polarization causes a difference in all the spin-up and spin-down valence wave functions and results in a small polarized charge density of -0.007 a.u. at each proton. This is only -2% of the charge density of a H atom *in vacuo*. Its magnitude is within a factor of 3 found experimentally for PtH_2 [10–12,14]. It is unclear whether this discrepancy is due to calculational errors or differences between Ni and Pt.

In conclusion, the calculations show that the substitutional Ni^- defect with T_d symmetry is unstable against a displacement along the $\langle 100\rangle$ axis. The t_2 gap level is split into b_1, b_2, and a_1 levels in ascending energy. Ni_s can complex with two H atoms at AB sites and act as a double acceptor. It gives two H LVMs around 2000 cm^{-1}. The polarization charge density is very small and negative at the H nuclei, and we suggest that PtH_2 complexes assume the same structure.

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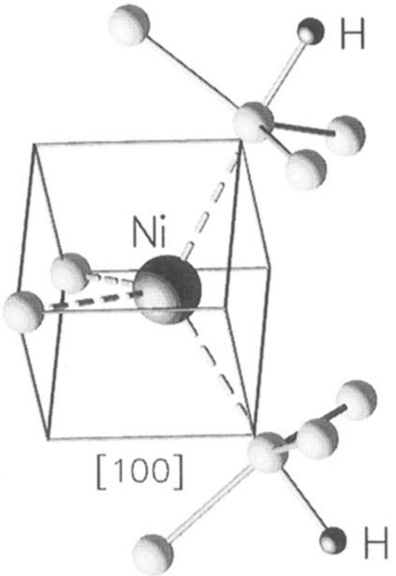

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