The structural properties of transition metal hydrogen complexes in silicon

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Abstract

A first-principles spin-polarised local density functional cluster method is used to explore the structural and vibrational properties of several substitutional transition-metal impurities complexed with hydrogen.

Key words: Ab initio theory, transition-metal impurities, H, Si.

1 Introduction

It is now a well-known fact that hydrogen can interact with transition-metal (TM) impurities, forming either electrically active or inactive complexes. An example of the former is the paramagnetic and orthorhombic $(PtH_2)^-$ defect, observed experimentally by electron-paramagnetic resonance and IR-absorption [4]. Despite the success with the Pt^- centre, experimental information on the structure and chemical composition of other $TM-H_n$ complexes is still rather sparse and inconclusive.

2 Methodology & results

Before presenting the results of the present study on the structural properties of TM-H_n complexes in Si, we describe the structure of the single substitutional TM impu-

rity. Non-relativistic spin-polarised local density functional theory is used, within a pseudo-potential real-space method (AIMPRO) to study the structural properties of substitutional, neutral gold (Au_s^0) and single negatively charged platinum (Pt_s^-), as well as the TM-H_n complexes with $n = 1$ and 2 for both impurities. Details on the method can be found elsewhere [3].

2.1 Substitutional Au^0 and Pt^-

For substitutional Pt^- and Au^0, there are three electrons in the one-electron t_2 manifold, which makes this state Jahn-Teller sensitive. Experiment and theoretical studies have shown that the JT-stabilised structures have C_{2v} symmetry, spin $S = 1/2$ for a ground-state configuration $b_2^{\uparrow\downarrow} b_1^{\uparrow} a_1^0$, in agreement with the vacancy model [1]. According to this model, the electronic properties of substitutional TM impurities near the end of the $3d$, $4d$ and $5d$ series can be described by considering a neutral TM atom with a saturated d^{10} shell occupying a negatively charged lattice vacancy. As a consequence, the structural and electronic properties of these impurities are dictated by the vacancy-like character of the sp^3 Si hybrid orbitals and not by the many-electron character of the partially filled TM nd shell.

The distortions have been investigated by breaking the symmetry and relaxing the Si inner atoms including the impurity, in a specific electronic configuration under the appropriate symmetry constraint [6]. The C_{2v} structures with the impurity displaced off-site along the dihedral [100] direction have proven to be stable with small shifts of the neighbouring Si atoms. The magnitude of distortion is slightly larger for Ni_s^- and Pt_s^- than for Au_s^0 or Ag_s^0. The equilibrium structures were found to correspond to a displacement of 0.20 Å for Ni^-, and 0.15 Å for Pt_s^-. For Au_s^0 and Ag_s^0, these were 0.03 and 0.01 Å, respectively. Our calculations find a small barrier for thermal re-orientation, consistent with experimental results for Pt_s^- and Au_s^0. In the case of Au_s^0 and Pt_s^0, the thermal barrier was calculated to be 0.11 and 0.26 eV, respectively.

An alternative model has been introduced to explain apparent discrepancies between the observed g values for Pt^- and those predicted by the vacancy model for the same centre. To test the predictions of the *two-neighbouring-bonding* or dihedral model [2], the TM ion was displaced off-site by 0.8 Å along the [100] direction, closer to two neighbouring Si, and the opposite Si atoms to the vacancy were brought closer, to simulate the stronger tetragonal distortion. For Pt_s^-, the TM ion moved back closer to its T_d site, to stabilise to within 0.01 Å of the lattice site, in evident disagreement with the predictions of the dihedral model.

2.2 TM-H_n complexes

Recent local vibrational-mode (LVM) spectroscopy studies [5] have revealed the existence of a gold-hydrogen defect, containing a single hydrogen atom in a C_{3v}

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symmetry. Two local vibrational modes have been identified, at 1813.3 and 1827.1 cm^{-1}, associated with two different charge states of the AuH$_1$ complex. These bands shifted by 502.4 and 507.7 cm^{-1} when hydrogen was replaced by deuterium, demonstrating unequivocally the involvement of hydrogen in the defect. Samples containing an admixture of H$_2$ and D$_2$ exhibit no additional vibrational bands. Despite these facts, it was impossible to identify the atom to which the H atom is bonded, along the <111> axis of the centre. However, recent studies indicate that the AuH$_1$ might have a lower symmetry of C$_{1h}$ [5].

Table I. Hydrogen stretch modes for AuH$_1$ complexes.
Observed isotope shifts are given in parentheses. Values in cm^{-1}.

(AuH$_1$)^q	$q = 0$	-1	-2	(AuD$_1$)^q	$q = 0$	-1	-2
Expt. [5] 1813.3 (1827.1) & 1310.9 (1319.4)							
BC	2419.0	2500.8	2454.3	BC	1726.2	1783.5	1748.9
AB$_{out}^{C_{1h}}$	1947.4	1890.5	1893.2	AB$_{out}^{C_{1h}}$	1401.1	1359.6	1361.4
AB$_{in}^{C_{1h}}$	2014.5	1980.0	2118.0	AB$_{in}^{C_{1h}}$	1427.3	1402.8	1500.2

To study the structural and vibrational properties of the AuH$_1$ defect, three structures were used, in three different charge states. These were: *a*) BC (with the H atom sitting *bond-centred* between the TM impurity and a Si atom; *b*) AB$_{out}$ (the H atom at the anti-bonding site to one of the Si neighbours) and *c*) AB$_{in}$ (H is inside the vacancy along the [111] direction. A lower symmetry AB$_{out}$ configuration was also considered, in which the bond between two of the vacancy Si neighbours was slightly reconstructed. The BC and AB$_{in}$ structures of the AuH$_1$ complex were found to be less stable than the AB$_{out}$ by 0.47 and 0.23 eV, respectively; the C$_{3v}$ and C$_{1h}$ AB$_{out}$ structures where found to be degenerate in energy. The Si–H length was 1.52 Å for both C$_{3v}$ and C$_{1h}$. For AB$_{in}$, the Au–H length was 1.60 Å. The calculated stretch LVM frequencies are given in Table I. In all the structures, the *off-site* displacement of the TM impurity atom is rather small. For AB$_{in}$, the Au moves off-site by 0.06 Å along [$\bar{1}\,\bar{1}\,\bar{1}$] and 0.02 Å along the [111] for AB$_{out}^{C_{1h}}$. The energy barriers for re-orientation between symmetric configurations were, 0.41 eV for AB$_{out}^{C_{1h}}$, and 0.23 eV for AB$_{in}$. These barriers are probably reduced by tunnelling.

The calculated quasi-harmonic local-vibrational modes (LVMs) for (PtH$_1$)$^-$ were 1830.0 and 1728.1 cm^{-1}, for AB$_{out}^{C_{1h}}$ and AB$_{in}$, respectively. Again, as in the case of AuH$_1$, the closeness between LVM does not identify the structure responsible for the vibrational band at 1897.2 cm^{-1} seen in hydrogenated Pt-doped Si and attributed to a (PtH$_1$) defect [4].

We now investigate (PtH$_2$)$^-$ and (AuH$_2$)^0. The structure of (PtH$_2$)$^-$ is consistent with experiment and previous modelling. The AB (C$_{2v}$) configuration was found to be more stable than the competing BC by 0.40 eV for (PtH$_2$)$^-$ and 0.53 eV for

$(AuH_2)^0$. The Si–H lengths were 1.54 and 1.52 Å, for the Pt-H and Au-H related defects, respectively. For $(PtH_2)^-$, the splitting between the calculated A_1 (1763.1) and B_1 (1756.2) modes was ~ 7 cm^{-1}, in fair agreement with the observed value of 19.4 cm^{-1} [4]. As expected, due to a shorter Si–H length, the stretch mode frequencies for the AB AuH_2 defect were 151.0 and 156.4 cm^{-1} higher than the Pt analogue.

3 Conclusions

In conclusion, the calculations show that Pt_s^- is unstable against a slight displacement along the <100> direction. Au_s^0 shows a similar structure, with a weaker JT distortion. For the TM-H_1 defects, the AB_{out} configurations were energetically favoured but the differences in energies with the AB_{in} configurations are not large. We tentatively assign the observed AuH_1 defect to the $AB_{C_{1h}}^{out}$ structure. As in previous theoretical studies [6], we have confirmed the AB structure as the most stable TM-H_2 defect structure, in which the two H atoms lie outside the vacancy.

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