THEORY OF THE NiH_2 COMPLEX IN Si AND THE CuH_2 COMPLEX IN GaAs

R. JONES [1], J. GOSS [1], S. ÖBERG [2], P. R. BRIDDON [3], and A. RESENDE [4]

[1] Department of Physics, University of Exeter, Exeter, EX4 4QL, United Kingdom

[2] Department of Mathematics, University of Luleå, Luleå, S95 187, Sweden

[3] Department of Physics, University of Newcastle Upon Tyne, Newcastle upon Tyne, NE1 7RU, United Kingdom

[4] Departamento e Centro de Física (INIC), Universidade de Aveiro, 3800 Aveiro, Portugal

Keywords: TM Impurities, Si, GaAs, Ni, Cu, H, theory.

Abstract. Spin-polarised local density functional cluster calculations are carried out on substitutional Ni in Si and Cu in GaAs along with TM-H_2 complexes. The Jahn-Teller distortion for Ni in Si leads to a slight displacement along $\langle 100 \rangle$ in agreement with EPR experiments. Several models of NiH_2 are investigated and it is shown that one, with H located at anti-bonding sites to two of the Si neighbours of Ni, has the lowest energy and possesses H related local vibrational modes close to those reported for Pt-H_2. A similar structure is found for CuH_2 in GaAs. The electronic properties of the complexes are described in terms of the vacancy model of TM impurities.

Introduction

Hydrogen can passivate shallow donors and acceptors yielding defects in which H lies at a bond centred (BC) site in the case of acceptors and anti-bonding (AB) sites for donors [1, 2, 3], although there are some exceptions to this, e.g. B in diamond [4]. Deep defects such as vacancies and interstitials can also complex with H. In the case of Si, the vacancy can be passivated [5] although in compound semiconductors like InP, VH_4 is a shallow donor [6]. Relatively little is known theoretically about the effects of H on transition metal impurities although early reports suggested that some could be passivated [7]. Recently, it was found that PtH_2 complexes introduce a second level lying above the E_c-0.23 eV acceptor level of Si:Pt_s. Pt forms several complexes with H, and one which is stable to 600°C contains two H atoms. EPR and IR measurements [8, 9, 10, 11, 12, 13] reveal that PtH_2 has C_{2v} symmetry. The hyperfine interaction with H is very weak and the defect has two close-by H localised vibrational modes (LVMs) around 2000 cm^{-1}.

In contrast with Si:PtH_2, H passivates Cu_{Ga} in GaAs [14]. DLTS studies [14] show that the activation energies 0.13 and 0.40 eV for single and double ionised Cu_{Ga} in GaAs are eliminated on exposure to a H plasma. The Cu acceptor has also been passivated by Li [15]. We have investigated the properties of both of these defects using a local density functional cluster method described below.

Method

The AIMPRO *ab initio* spin-polarised local density functional cluster theory [16] code is used, with tetrahedral H-terminated clusters containing 133 atoms in the configuration $NiSi_{70}H_{62}$

for NiH_2 defects in Si, and $CuGa_{30}As_{40}H_{62}$ for CuH_2 defects in GaAs. The basis consists of N Gaussian s,p-orbitals sited on each atom and the charge density is fitted to M Gaussian functions. Here (N,M) for each atom are: Ni(7, 14), Cu(7, 14), H(2, 3), Si(4, 5), Ga(4, 5) and As(4, 5). N independent d-orbitals were sited on Ni and Cu. In addition, bond-centred s- and p-Gaussians were placed at the centres of the innermost bonds. The charge density was expanded in M independent s-Gaussian functions together with functions placed at bond centres. The pseudo-wavefunctions were expanded in independent combinations of the N Gaussian orbitals sited on atoms at the centre of the cluster have but a fixed linear combination of basis orbitals is used on those outside the core. The pseudopotentials of Ref. [17] were placed on all atoms except H. An important aspect to the method is that the forces are calculated on each atom and the cluster relaxed until the equilibrium one is found. These forces can be differentiated and hence the dynamical matrix of the cluster found as described earlier [16]. Tests carried out showed the method reproduced the bond lengths of $Ni(CO)_4$ and CuH to within 1%.

Ni_s^- and Ni_s^--H_2 Defects in Si

Substitutional Ni^- placed at the centre of a 71 atom tetrahedral cluster possessed a deep t_2-level filled with three electrons. We investigated the experimentally observed S=1/2 configuration for which the T_d symmetry is unstable [18]. We found that Ni moved 0.13 Å along [100] with C_{2v} symmetry and the t_2 level split into three levels: $b_1^{\uparrow\downarrow} b_2^{\uparrow} a_1^0$. The energy separation between $b_2^{\uparrow}$ and $b_2^{\downarrow}$ is about 0.6 eV but there is only a small splitting between the $b_1^{\uparrow}$, $b_2^{\uparrow}$ and a_1^0 levels. This ordering of energy levels agrees with uniaxial stress measurements [19] and is the reverse to that found in V^-. The $b_2^{\uparrow}$ wave-function has lobes near the anti-bonding sites to the Si neighbours and near to the nodal surface around the mid-point of the Ni-Si bond. This suggests that H will attack the defect and lie preferentially at these sites.

Several candidate structures for $Ni_s^- H_2$ were investigated. In the lowest energy one, Fig. 1, the H atoms lie at AB sites to two of the Si neighbours of Ni_s. The Si-H bonds are 1.557 Å and the H-H separation is 7.3 Å. The H stretch modes are given in Table 1. There are two modes around 2000 cm^{-1} and are split by 7 cm^{-1}. These are close to the modes of PtH_2. The higher is an A_1 mode involving the motion of the two H atom in phase with each other, and the lower is a B_1 mode where the H atoms move put of phase. This ordering of modes is in agreement with observations on PtH_2 where the modes are are split by 13 cm^{-1} [9].

The highest occupied gap state has $b_2^{\uparrow}$ symmetry whose energy lies around mid-gap and an unoccupied $b_2^{\downarrow}$ state lying in the upper half of the gap. This second acceptor level is found around $E_c - 0.1$ eV in the case of PtH_2. The pseudo-wavefunction of the $b_2^{\uparrow}$ state reveal a nodal plane running through the Si-H bonds. Thus there is very little spin-polarisation at the H nuclei. The calculations give the polarisation density to be negative and 2% of that of the H atom in vacuo. This quantity is also observed to be very small for PtH_2 — about 0.6% of H. Recently, Uftring et al [13] estimated the Pt-H distance to be 4.3 Å from the anisotropic hyperfine parameter. This is consistent with AB sited model as we find a Ni-H distance of 4.5 Å. We also note that the H stretch modes are far below those of VH_2 [5] consistent with the weaker p-bond appropriate for H located at the AB site. All these results suggest that the H atoms are located at AB sites although the model gives bend modes around 900 cm^{-1} which so far remain undetected.

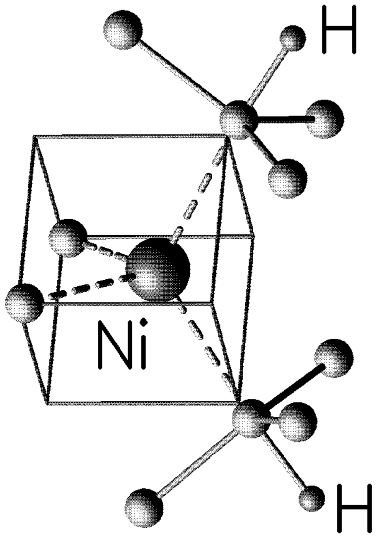
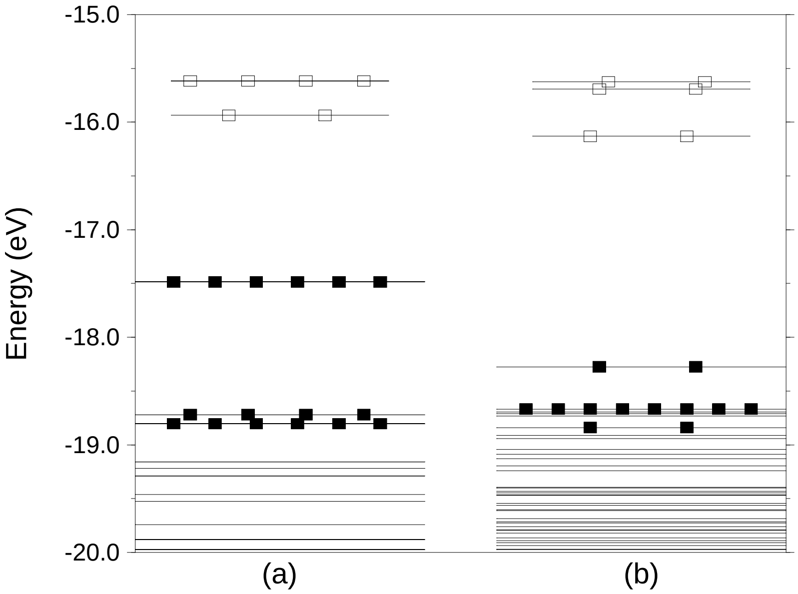


Fig. 1: A schematic representation of the lowest energy NiH_2 complex in Si, with the H-atoms in the anti-bonding (AB) site.

Fig. 2: A plot of the electronic structure (Kohn-Sham eigenvalues) for (a) substitutional Cu^{--} and (b) CuH_2 in GaAs. The filled boxes signify filled levels, and the empty boxes unoccupied states. Only states in the region of the gap have been plotted. It can be clearly seen how the addition of H to Cu pushes the gap states down towards the valence band, passivating the defect.



Cu_{Ga}-H_2 Defect in GaAs

Cu is known to act as a double acceptor in GaAs which can be passivated by H [14] or Li [15]. Cu_{Ga}^{2-} lies on site but repels its four neighbours outward so that the Cu-As bonds have length 2.69 Å. There is an occupied triplet t_2-level around mid-gap [20] illustrated in Fig. 2 (a). We investigated two models of the CuH_2 defect possessing C_{2v} symmetry in analogy with NiH_2 defect in Si.

In the AB sited defect, Cu is displaced 1.1 Å along [100] towards the H atoms. The As-H bonds were 1.58 Å and the four Cu-As lengths are 2.62 Å and 2.90 Å. The triplet level is split and pushed downwards towards the top of the valence band (Fig. 2b). The frequencies of the

H stretch modes are given in Table 1. There are no reports of these modes to-date. The highest modes are split by 3 cm^{-1} with the higher mode of A_1 symmetry as in NiH_2 in Si.

In an alternative configuration, the H atoms were placed far-apart from each other inside the vacancy. The energy of the relaxed cluster is 0.1 eV higher than the AB sited one. Hence, once again there is a preference for H to occupy AB sites outside the vacancy cage.

The energy levels are very similar to those of the AB sited case: namely that the gap appears free from levels. The H-stretch modes are now much higher at 2325 and 2317 cm^{-1} with the B_1 mode the higher of the two.

Table 1: Calculated Vibrational Modes [cm^{-1}] for TM-H_2^- AB defects

Calculated						
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. [9, 10, 13]						
Pt H_2	1901.6	1888.2	-	-	-	-
Pt HD	1894.6	1366.9	-	-	-	-
Pt D_2	1370.7	1362.5	-	-	-	-
Calculated						
Cu H_2	2139.9	2136.8	991.6	989.2	755.8	724.3
Cu HD	2139.4	1523.1	990.4	741.0	703.2	524.4
Cu DD	1524.2	1521.9	704.0	702.3	536.4	514.3

Conclusions

The calculations show that H does not form bonds with the TM impurities directly but bond to bulk atoms surrounding the impurity. In the cases considered here, there is a small extra binding energy for H to be located at anti-bonding sites. Levels are introduced into the gap in the case of Si:Ni but removed from the gap in the case of GaAs:Cu_{Ga}. As yet, we do not possess a general theory of the effects of H on TM impurities and further calculations are required.

Acknowledgements

S. Öberg thanks NFR and TFR in Sweden for financial support. He also thanks PDC at KTH in Sweden, for computer time on the SP2. We also thank the HPCI committee of the EPSRC for computer time on the T3D where some of these results were obtained. R. J. thanks G. D. Watkins, M. J. Stavola and S. Uftring for useful discussions.

References

[1] C. G. Van de Walle, *Deep Centers in Semiconductors: a state-of-the-art approach*, ed S. T. Pantelides, Gordon and Breach, Switzerland, pp. 928, 899-928, (1992).

[2] S. K. Estreicher, Mat. Sci. Engr. Reports 14, June (1995).

[3] R. Jones, Phil. Trans. Roy. Soc. Lond. A **350**, 189, (1995).

[4] S. J. Breuer, and P. R. Briddon, Phys. Rev. B **49**, 10332 (1994).

[5] B. Bech Nielsen, L. Hoffmann, M. Budde, R. Jones, J. Goss, and S. Öberg, this conference.

[6] C. P. Ewels, S. Öberg, R. Jones, B. Pajot, P. R. Briddon, this conference.

[7] S. M. Myers, M. I. Baskes, H. K. Birnbaum, J. W. Corbett, G. G. DeLeo, S. K. Estreicher, E. E. Haller, P. Jena, N. M. Johnson, R. Kirchheim, S. J. Pearton, and M. J. Stavola, Rev. Mod. Phys. **64**, 559-617 (1992).

[8] P. M. Williams, F. S. Ham, F. G. Anderson, and G. D. Watkins, Mater. Sci. Forum, **83-7**, 233 (1992).

[9] P. M. Williams, G. D. Watkins, S. Uftring, and M. Stavola, Phys. Rev. Lett. **70**, 3816 (1993).

[10] P. M. Williams, G. D. Watkins, S. Uftring, and M. Stavola, Mater. Sci. Forum **143-7**, 891 (1994).

[11] M. Höhne, U. Juda, Yu. V. Martynov, T. Gregorkiewicz, C. A. J. Ammerlaan, and L. S. Vlasenko, Mater. Sci. Forum, **143-7**, 1659 (1994).

[12] M. Höhne, U. Juda, Yu. V. Martynov, T. Gregorkiewicz, C. A. J. Ammerlaan, and L. S. Vlasenko, Phys. Rev. B **49**, 13423 (1994).

[13] S. J. Uftring, M. Stavola, P. M. Williams, and G. D. Watkins, Phys. Rev. B **51**, 9612 (1995).

[14] G. Hoffmann, J. Madok, N. M. Haegel, G. Roos, and N. M. Johnson, and E. E. Haller, Appl. Phys. Lett. **61**, 2914 (1992).

[15] T. Egilsson, H. P. Gislason, and B. H. Yang, Phys. Rev. B **50**, 1996 (1994).

[16] R. Jones, Phil. Trans. Roy. Soc. London A **341**, 351 (1992).

[17] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[18] L. S. Vlasenko, N. T. Son, A. B. van Oosten, C. A. J. Ammerlaan, A. A. Lebedev, E. S. Taptygov, and V. A. Khramtov, Solid State Comm. **73**, 393 (1990).

[19] F. G. Anderson, F. S. Ham, and G. D. Watkins, Phys. Rev. B **45**, 3287 (1992).

[20] R. Jones, and S. Öberg, Semicon. Sci. and Technol. **9**, 2291 (1994).