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1991 J. Phys.: Condens. Matter 3 4373

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J. Phys.: Condens. Matter 3 (1991) 4373–4379. Printed in the UK

The interstitial hydrogen atom in gallium phosphide

K F Wong, G S Khoo and C K Ong
Department of Physics, National University of Singapore, Kent Ridge, Singapore 0511

Received 4 February 1991

Abstract. In the present work, we have calculated the energy profiles of a hydrogen atom located at different positions on the (110)-plane in GaP by employing the CNDO method. The actual global minimum is found when the hydrogen atom lies at a site at a distance 1.44 Å away from the nearest P atom along the ⟨001⟩-axis on the (110)-plane. This distance is very close to the P–H bondlengths of 1.43 and 1.42 Å in the PH and PH_3 molecules respectively.

1. Introduction

The prevalent use of Si and Ge in the semiconductor industry has prompted numerous research studies on these two materials. The literature on Si and Ge is therefore prolific whereas data on other semiconductors [1] e.g. the III–V compounds especially with regards to theoretical work are scarce. Interest in recent years, however, has been shifting towards the III–V compounds because of the potential they promise. Scientists are turning to compound semiconductors like GaP for solutions and alternatives because of the problems and limitations in economy of time which have arisen, for example, in the use of purely elemental Si and Ge as semiconductor materials. The III–V compounds have also displayed tremendous theoretical potential for heterostructure transistor technology [2] which is increasing in importance. Such technology, which incorporates the heterostructures into most existing kinds of device, enhances their performances. But again, this current interest in III–V compounds is surprisingly not matched by any corresponding theoretical data, say, on impurities like H in such compound semiconductors. In fact, almost nothing is known about the states of hydrogen in compound semiconductors [1].

Hence, there exists a great need for more theoretical and experimental work to establish models for the influence of impurities in such semiconductors. It is with this aim in mind that our work here focuses on the properties of H in GaP so that our results may shed more light on the understanding and interpretation of the behaviour of these compound semiconductors.

2. Theoretical tool

In order to study the properties of interstitial H in GaP, we use the complete neglect of differential overlap (CNDO) method which entails that we must first obtain a suitable set of CNDO parameters for GaP [3].

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The CNDO method is a semi-empirical self-consistent molecular orbital theory whereby approximations are systematically applied to the matrix elements of the Hartree–Fock–Roothaan equations. These approximations are introduced in three semi-empirical parameters: the orbital exponent (ξ), the electronegativities (ε) and a bonding parameter (β). The final results of the CNDO calculations yield self-consistent solutions similar to Hartree–Fock solutions as well as predicting the total energy of the system. Here, we use the Harwell MOSES code [4] to perform our calculations and this method has been used successfully on hydrogen in diamond and Si [5], hydrogen in Ge [6], self-interstitials in Si and Ge [7, 8] and hydrogen complexes in Si [9, 10].

The parameters we have used here are illustrated in table 1. The H parameters are from Pople and Beveridge [3] while the parameters for GaP are those we have obtained through the procedure described below. In our parameterization procedure for GaP, we perform our calculations on a 16-atom periodic large unit cell (LUC) of GaP. Essentially, we vary the parameters starting from the values obtained from the standard method as proposed by Pople and Beveridge [3] until they result in calculated values of the valence bandwidth, cohesive energy and interatomic spacing which are in good agreement with their experimental values. This procedure is similar to the one adopted by us for Ge [11] as well as by Harker and Larkins for Si [12].

Table 1. The CNDO parameters used.

Atoms	Electronegativity (eV) ε_s	ε_p	Bonding parameter (eV) β	Orbital exponent (Bohr^{-1}) ξ
Ga	5.22	4.43	−1.2	1.80
P	11.20	5.20	−10.5	1.65
H	7.18	—	−9.0	1.2

Table 2. Comparison of predicted bulk properties of GaP crystal with experimental data.

Bulk properties	Calculated	Experiment
Valence bandwidth (eV)	14.13	13.2 ± 0.4 [13]
Cohesive energy (eV) per bond	1.71	1.78 [14]
Equilibrium inter-atomic spacing (Å)	2.42	2.36 [15]
Mulliken charge densities on		
P atom	$s^{1.70}p^{3.38}$	
Ga atom	$s^{0.52}p^{2.40}$	

The optimum set of CNDO parameters we obtained for GaP have already been listed in table 1 as mentioned earlier. The calculated values for the three bulk properties, namely the valence bandwidth, the cohesive energy and internuclear distance, as well as Mulliken charge densities on Ga and P atoms, obtained with this set of parameters together with the experimental data are presented in table 2. Our results are in fairly

good agreement with experiment and in the subsequent sections, the results for H in crystalline GaP will be presented with the help of these parameters.

3. Procedure

3.1. Cluster description

In our approach, we study the properties of interstitial H in GaP by using clusters of Ga and P atoms to simulate the crystalline structure of GaP. The dangling bonds at the edges of these clusters are saturated either by hybrid atoms of Ga or P at locations representing the next shell of neighbours. These hybrid or pseudoatoms have their parameters modified to imitate single hybrid Ga or P orbitals. Most of the studies are performed on two 70-atom clusters, both centred at tetrahedral (T) sites (see figure 1). One cluster has Ga atoms as the nearest neighbours of the T-site while the other has P atoms as the nearest-neighbours. These clusters are similar to those used by us for Ge [6] and by Mainwood and Stoneham for Si [5] to study the properties of interstitial H.

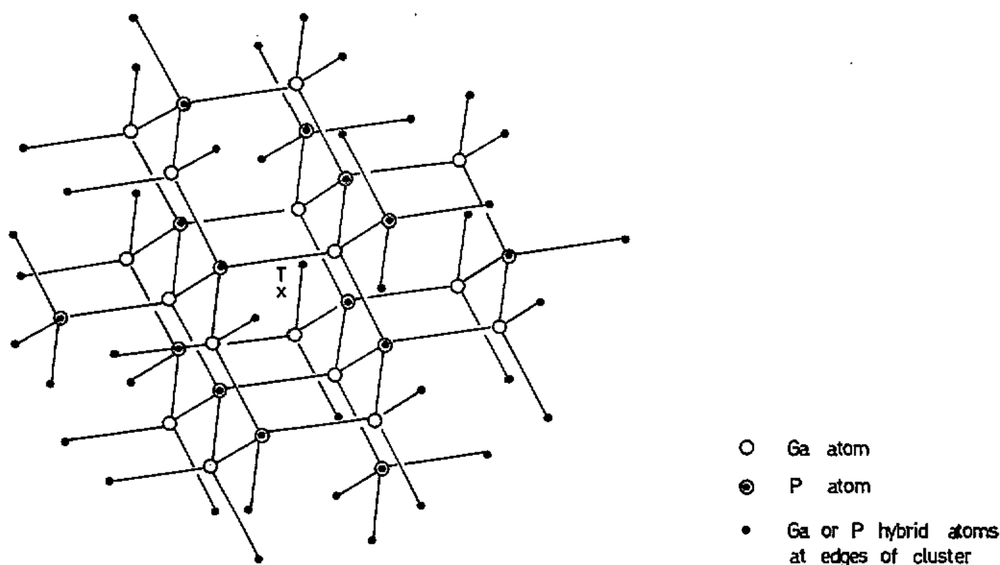

Figure 1. Tetrahedral-centred cluster used in our calculations. T is the centre of the cluster (T is a tetrahedral site). This cluster has Ga atoms as the nearest-neighbours of the T-site.

3.2. Main interstitial locations

The prominent interstitial sites of interest like the T-site, hexagonal (H)-site, and the antibonding (AB)-site are located on the (110)-plane of the diamond lattice of GaP. Most of our calculations are performed on this plane especially along the ⟨111⟩-direction. This axis contains two T-sites (one surrounded by Ga nearest-neighbours and the other by P), a H-site in between as well as the AB-site as shown in figure 2. For the major part of our work, we use this plane and axis to construct the energy profiles of interstitial H in GaP.

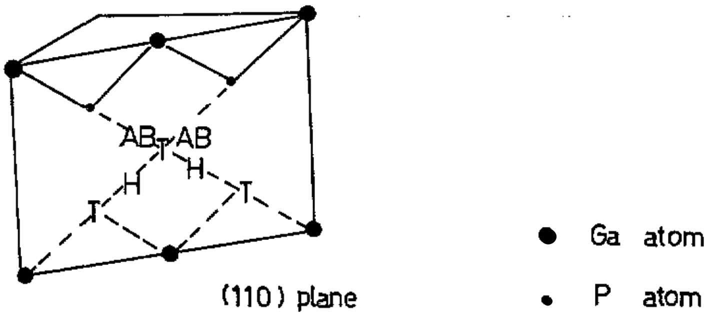

Figure 2. The (110)-plane where most of our calculations are performed. The major interstitial sites on this plane like the antibonding (AB), tetrahedral (T) and hexagonal (H) sites are also labelled. Large dots, Ga atom; small dots, P atom.

3.3. Calculations

We first perform our calculations on the T-centred cluster with Ga atoms as nearest-neighbour. The H atom is moved along the major axes on the (110)-plane around the vicinity of the central T-site. The other T-site with P atoms as nearest-neighbour is a distance away from this central T-site so the calculations are repeated on the cluster with the P atoms as nearest-neighbours. All our calculations are performed for the case of no lattice-relaxation around the H atom.

4. Results

Figure 3 illustrates the variation of the total energy of the GaP cluster with the H atom moving along the ⟨111⟩-axis from one of the Ga atoms nearest to the central T-site. The profile of the plot suggests strongly that the H atom localizes itself at the AB-site along the backbond direction from a Ga atom. However, this AB-site is just a local minimum. Movement of the H atom away from this site along the ⟨011⟩-axis leads to high energy indicating that diffusion along this axis is not favoured. However, when the H atom is moved along the ⟨001⟩-axis from the AB-site, another position of minimum energy is attained. This site labelled X_{Ga} is indicated in figure 4(*a*). The barrier for diffusion from the AB-site to X_{Ga} is about 1.2 eV (see figure 4(*b*)). The hump in figure 4(*b*) along the ⟨001⟩-axis can possibly be bypassed if the H atom diffuses along another path to reach X_{Ga} which is the global minimum of the H in GaP with Ga atoms as the nearest-neighbours of this defect site (X_{Ga}).

The calculations are then repeated under the same circumstances for H in the interstitial space around the second T-site with P atoms as the nearest-neighbours in the second cluster. Figure 5 illustrates the energy profile of the H atom along the ⟨111⟩-axis in the vicinity of the P atoms for this set of calculations. Once again, the local minimum along the ⟨111⟩-axis is the AB-site, a slight distance along the backbond direction from one of the nearest-neighbour P atoms of the central T-site. Movement of the H atom along the ⟨011⟩-axis from this site leads to high energy again, showing its non-preference for this direction. Similarly, when the H atom is moved along the ⟨001⟩-axis from this AB-site, another position of minimum energy (X_P) is found (see figure 6(*a*)). This is analogous to X_{Ga} in the previous case for Ga atoms as nearest-neighbours. Figure 6(*b*) illustrates the total energy curve for diffusion of the

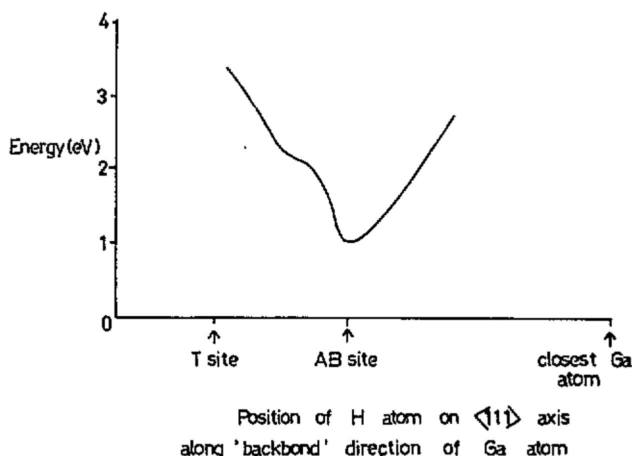

Figure 3. Energy profile of the H atom as it moves along the 'backward' direction of a Ga atom close to a T-site.

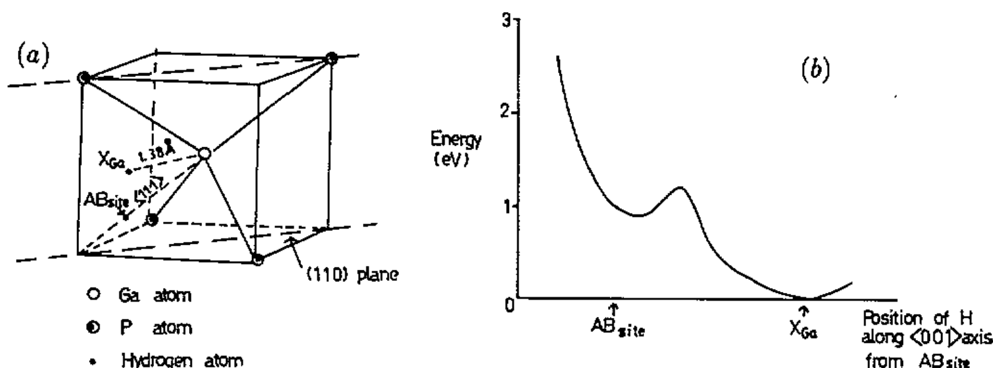

Figure 4. (*a*) Diagram showing the location of X_{Ga} with respect to the AB-site on the (110)-plane. (*b*) The total energy profile of the H atom as it moves from the AB-site to X_{Ga} along the ⟨001⟩-direction. X_{Ga} is set at the lowest energy.

interstitial H atom from the AB-site to X_P. The shape of this energy profile is similar to that for the Ga case except that the hump in figure 4(*b*) between the AB-site and X_{Ga} is replaced by a more plateau-like barrier in figure 6(*b*). X_P is lower than X_{Ga} by about 1.5 eV, indicating that it is the actual global minimum for the system of interstitial H in GaP.

5. Discussion

The energy minimum for X_P is about 1.5 eV less than that for X_{Ga}, suggesting that interstitial H prefers to reside in the vicinity of the P atoms, rather than Ga atoms. There are several possible reasons for this. When H is at X_P, the H–P distance from its nearest P atom is 1.44 Å. This compares favourably with the equilibrium bondlength of 1.42 Å for P–H in PH_3 molecule [15]. In the case of Ga atom as the nearest-neighbour (X_{Ga}), the H–Ga distance is 1.38 Å whereas the experimental Ga–H bondlength [15] is much smaller (1.12 Å). However, both GaH and GaH_3 are known to be unstable

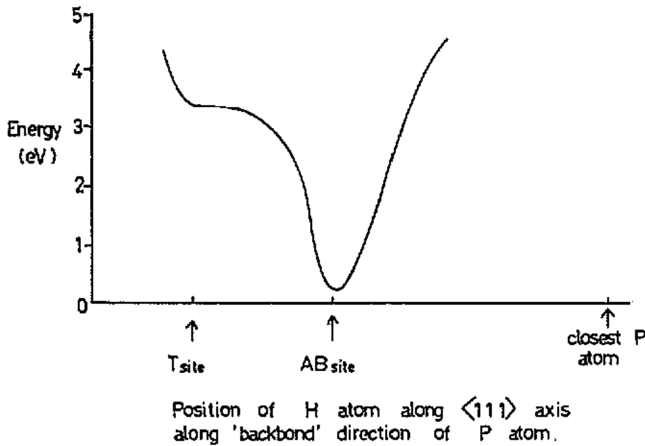

Figure 5. Total energy profile of the H atom as it moves along the 'backward' direction of a P atom close to the T-site.

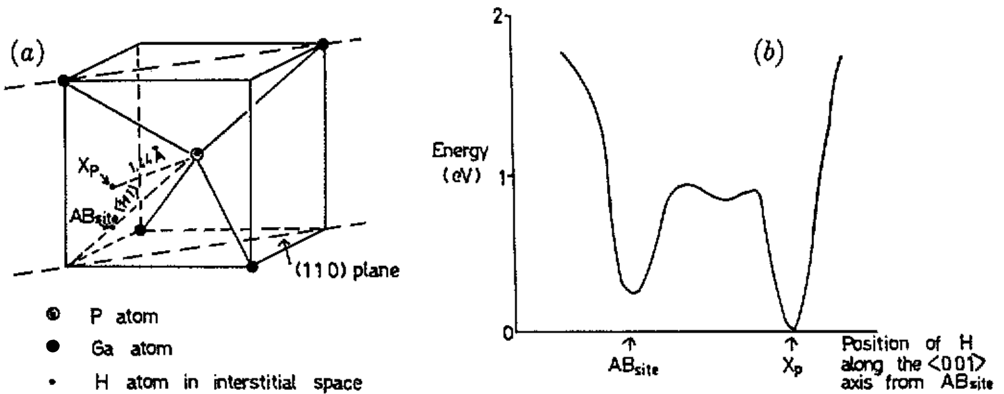

Figure 6. (*a*) Location of X_p with respect to the AB-site on the (110)-plane. (*b*) Total energy profile of the H atom as it moves from the AB-site to X_p along the ⟨001⟩-direction. X_p is set at the lowest energy.

molecules. This incompatibility in bondlength as well as the unstable nature of the Ga–H bond suggest that it is unlikely for an interstitial H to bond with one of the Ga atoms. Hence, we can conclude from the close agreement for the calculated P–H bondlength with experiment that in the vicinity of the P atoms, an interstitial H atom is most likely to form a bond with a P atom leading to a global minimum situation.

To date, there does not seem to be any experimental work on H in GaP with which we can compare our results. However, some experimental work on muonium in GaP [16] has led to the speculation that, in GaP, muonium (a hydrogen-like atom) may reside at the T-site with Ga atoms as nearest-neighbours. Our results are therefore not in agreement with their speculation. Our work suggests that the most likely site for occupation by an interstitial H atom is not a T-site but a location along the ⟨001⟩-direction on the (100)-plane at a distance of 1.44 Å from the nearest P atom. We believe our results are more reasonable because both GaH and GaH_3 are unstable while PH and PH_3 molecules are stable [15] indicating that a site near Ga atoms may not be the most favourable for occupation by the interstitial H atom. It is hoped

that more experimental and theoretical work on the diffusion of H in GaP will be forthcoming to shed more light on the understanding of this problem.

References

[1] Pearton S J, Corbett J W and Shi T S 1987 *Appl. Phys.* A **43** 153
[2] Kroemer H 1980 *Proc. 12th Conf. on Solid State Devices, Tokyo*; 1981 *Japan. J. Appl. Phys.* **20** suppl. 20–1 9
[3] Pople J A and Beveridge D L 1970 *Approximate Molecular Orbital Theory* (New York: McGraw-Hill)
[4] Harker A H and Lyon S B 1979 Harwell Report AERE R8598
[5] Mainwood A and Stoneham A M 1983 *Physica* B **116** 101
[6] Khoo G S and Ong C K 1987 *J. Phys. C: Solid State Phys.* **20** 1385
[7] Khoo G S and Ong C K 1987 *J. Phys. C: Solid State Phys.* **20** 5037
[8] Khoo G S and Ong C K 1990 *J. Phys. Chem. Solids* **51** 1177
[9] Ong C K and Khoo G S 1987 *J. Phys. C: Solid State Phys.* **20** 419
[10] Ong C K and Khoo G S 1991 *J. Phys.: Condens. Matter* **3** 675
[11] Ong C K and Khoo G S 1988 *J. Phys. Chem. Solids* **49** 883
[12] Harker A H and Larkins F P 1979 *J. Phys. C: Solid State Phys.* **12** 2489
[13] Ley L, Pollak R A, McFeely F R, Kowalczyk S P and Shirley D A 1974 *Phys. Rev.* B **9** 600
[14] Harrison W A 1980 *Electronic Structure and the Properties of Solids* (San Francisco: W H Freeman) p 176
[15] Bailar J C, Emeleus H J, Nyholm Sir R and Trotman-Dickenson A F 1973 *Comprehensive Inorganic Chemistry* vol 1, 75 1075; vol 2, 414 (Oxford: Pergamon)
[16] Kiefl R F, Schneider J W, Keller H, Kundig W, Odermatt W, Patterson B D, Blazey K W, Estle T L and Rudaz S L 1985 *Phys. Rev.* B **32** 530