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INTERSTITIAL MUONS AND HYDROGEN IN CRYSTALLINE SILICON

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We have calculated self-consistent total energy surfaces for H^+, H^o and H_2 present interstitially in crystalline Si. We conclude molecular hydrogen is the stable form, consistent with the lack of observed electrical and optical activity. Both H^+ and H^o have complex surfaces, with some features sensitive to lattice distortion. The local minima are too small to give localised states when zero-point energy is included. We discuss our results in relation to earlier theories and to experiments on "normal" and "anomalous" muonium $[\mu^+e^-]$.

1. INTRODUCTION

Experimental data on hydrogen in silicon are reasonably abundant, apparently mutually incompatible, and unexplained by current theories. One would expect hydrogen, deuterium, and muonium (μ^+e) to behave in similar ways since they are chemically identical and only differ in mass, but the most important experiments show instead:

(i) Hydrogen is electrically and optically inactive.

(ii) Muonium [1] (μ^+e, the analogue of hydrogen) appears to be present in two forms - normal muonium, Mu, with a compact s-like wavefunction on a site with tetrahedral symmetry, and anomalous muonium, Mu*, with <111> axis p-like anisotropic hyperfine structure. There appear to be transitions between the two states with a peculiar temperature dependence. It is possible that an excited or complex state, for example $[\mu^+e\ eh]$ is involved.

(iii) Implanted deuterium appears [2] to be displaced off the tetrahedral site towards a <111> back bond direction (although it may be associated with a defect).

Experiments on diamond and germanium complicate the matter further. Hydrogen is extremely abundant and very mobile in diamond [3]. Pion experiments in germanium [4] show a change of site at about 60°K for the π^+ from an off centre position (T $\sim$ 60K) to a central tetrahedral position. However, few defect properties have proved to be similar through the group IV crystals, so these observations may not have parallels in silicon. We shall describe elsewhere some similar work on diamond to which the reader is referred for a fuller discussion.

Current theories [5] do not account for these observations, and in most cases the reason is that they concentrate on the one-electron energy levels of the hydrogen constrained at the tetrahedral site. It is surely necessary to use a self-consistent procedure to calculate total energy surfaces, and from them attempt to explain the observed features.

2. THEORETICAL METHOD

The main ingredients of our approach are a self-consistent, though semi-empirical method, and a finite cluster approximation.

The CNDO (Complete Neglect of Differential Overlap) method.

We use a self-consistent, semi-empirical molecular orbital method, called CNDO [6]. It was devised for use on organic molecules, but can easily be parameterised and modified for use on solids, retaining the physical and chemical ideas The following approximations are made to the Hartree-Fock-Roothaan equations:

(i) Valence electrons alone are treated;

(ii) Matrix elements are approximated systematically using three types of parameter: electronegativity, orbital exponents and bonding parameters. The silicon parameters were obtained by Harker and Larkins [7], to fit the cohesive energy, lattice parameter and valence band width of a periodic cluster of silicon. The hydrogen parameters are those of Pople and Beveridge.

	Electro-negativity (eV)		Orbital exponent (au^{-1})	Bonding parameter (eV)
	s	p		
H	7.18	-	1.2	-9.0
Si	6.3	4.5	1.54	-6.4

Table 1. CNDO parameters used.

The code (here the Harwell MOSES [8] code)predicts the total energy for any chosen geometry, the one electron levels and wavefunctions, and other properties such as charge densities and matrix elements.

The method has been used successfully on vacancies [9], self-interstitials [10] and impurities [11] in diamond, to mention only related applications.

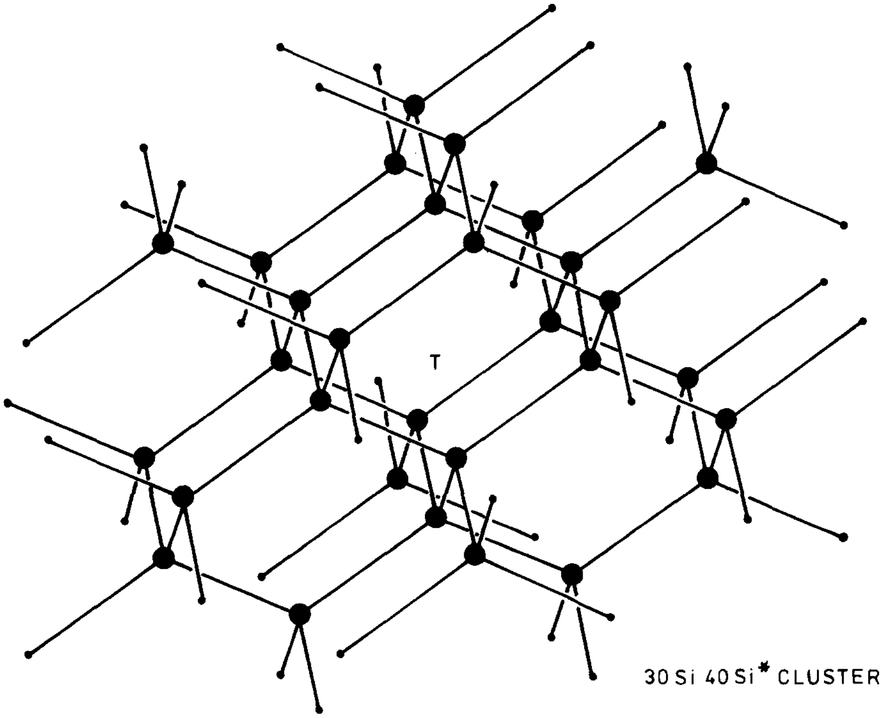
Clusters

We have taken clusters of silicon atoms of the correct lattice structure, with the dangling bonds at the surface of the clusters saturated by single sp^3 hybrids of silicon (Si*) at the correct positions to represent the next shell of neighbours. The (30 Si 40 Si*) cluster, used predominantly, is centred on a tetrahedral site, and includes seven shells of atoms.

Further calculations using a (29 Si 30 Si*) cluster showed that the effects of the hydrogen interacting with the cluster surface were not significant.

Total Energy surfaces for hydrogen in silicon.

By doing repeated calculations with hydrogen moved within the silicon cluster, with total charge zero, it is possible to build up the energy surface for hydrogen (or muonium) in silicon. If we put a net charge of +1 on the cluster we obtain the energy surface for H^+ (or μ^+).

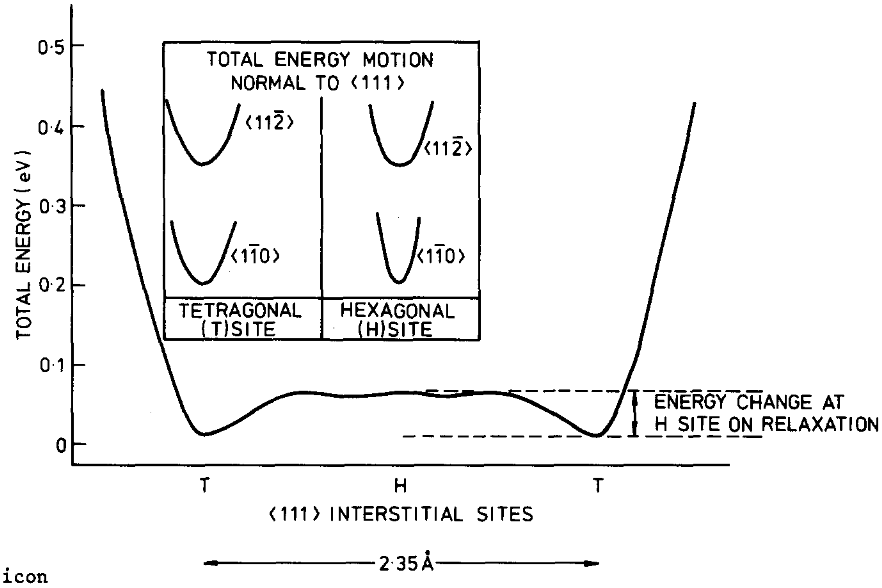


30 Si 40 Si* CLUSTER

3. RESULTS

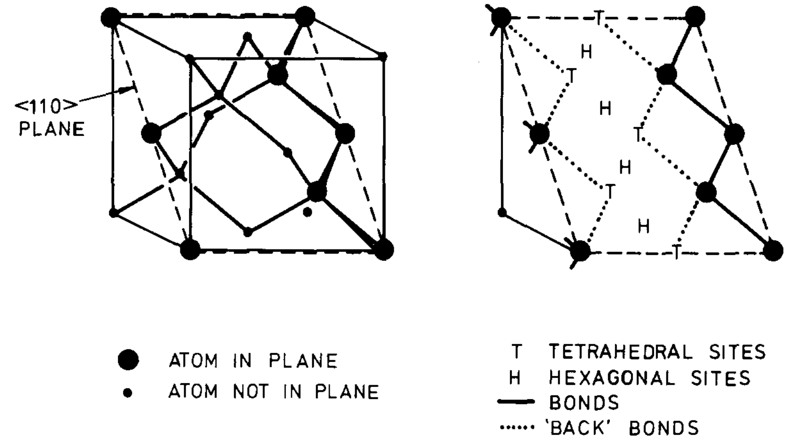
$H^o(\mu^+e)$ in Silicon

The hydrogen has an almost spherical potential well centred on the tetrahedral site, with narrow low energy channels via hexagonal sites to the next tetrahedral sites. The energy barrier is only .052 eV. However, if neighbouring silicon atoms are allowed to relax by only 1% of a lattice spacing the energy barrier is completely removed.

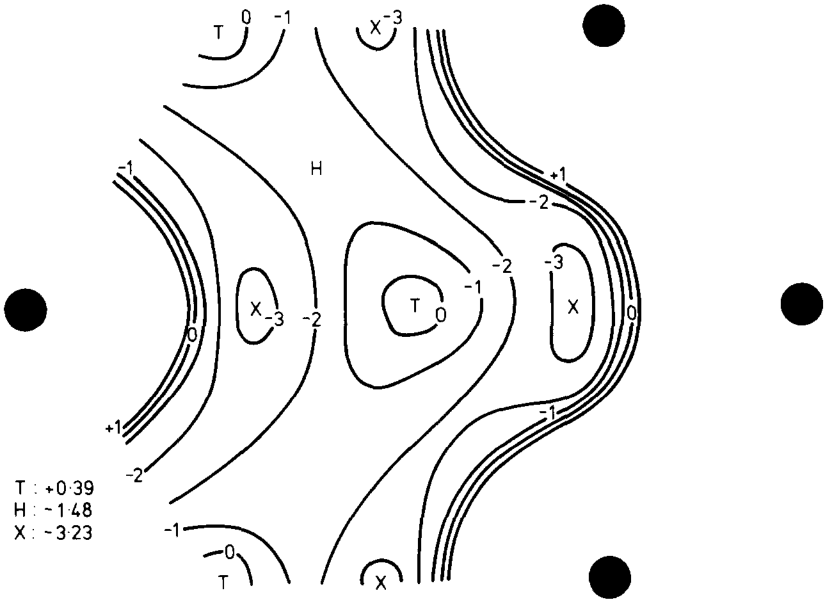


H^+ (μ^+) in Silicon

A <110> plane is used to show this energy surface



This energy surface is completely different from neutral hydrogen. The tetrahedral and hexagonal sites are high in energy with the minima along <001> directions about 1.6Å from a silicon atom. There is a saddle point between these sites along the back bond direction, but a direct route out of the <110> plane between minima associated with different tetrahedral sites gives a saddle point energy of only 0.21 eV. The potential well around the site X, is not harmonic but has a slight double minimum 7 meV lower. A simple variational calculation of zero-point energy in this well shows that the proton is barely bound and the muonium is certainly not bound in such a well.



$H^+(\mu^+)$ IN Si ⟨110⟩ PLANE

Molecular hydrogen (H_2) in silicon

Here we took the hydrogen molecule with its free spacing and placed it in the cluster at the tetrahedral site with [001], [110] and [111] orientations, and also straddling the hexagonal site along a [111] axis. Of these the tetrahedral [001] orientation was most stable, and further calculations showed that the free spacing was also correct. The barrier to rotation via a [110] axis is only 0.093 eV and the barrier to migration is .95 eV, although both these figures will be reduced substantially by lattice relaxation. The experimental activation energy for hydrogen diffusion is .5 eV to .6 eV.

Molecular hydrogen is more stable than atomic hydrogen by about 2 eV/atom in silicon, which is consistent with the complete lack of optical, infra-red and electrical activity of hydrogen in crystalline silicon.

4. DISCUSSION

Our calculations show how complex the energy surfaces of hydrogen or muonium in silicon are. It is clearly completely misleading to presume that the muon is trapped at a tetrahedral site and to base predictions on that assumption.

The wells are so shallow that there are apparently no localised states for muonium, $[\mu^+ e]$, and probably not for hydrogen. The muonium could be in a tunnelling state between a small number of sites, possibly with some self-trapping by the crystal, or loosely associated with a defect.

The energy surfaces are strongly dependent on charge state. We would not expect them to be quite so strongly affected by additional weakly-bound carriers in diffuse orbits around the hydrogen. For example a trapped exciton state like $[\mu^+ e\ eh]$ may have a similar energy surface to that for $[\mu^+ e]$. However, the fine structure and the radical differences between the μ^+ and $[\mu^+ e]$ surfaces demands reservation in detail. Since the lifetime of the muon is only 2 μsec, it is quite possible the observed Mu and Mu* species correspond to transient or metastable states, possibly involving bound excitons.

Finally, there are four remaining questions arising from the experimental muon spin rotation work, which these energy surfaces may help us to answer:

(a) Does the same model apply to diamond, Si and Ge? The hyperfine constants do not change monotonically along the sequence, which should make one suspicious of premature assumptions.

(b) Are impurities or defects involved? It is becoming accepted that simple donors and acceptors have only secondary influence [12,13], but transient defects caused by the muon may be involved during the muon's short lifetime, [14,15], even though the crystal may recover rapidly.

(c) Is the muon in a tunnelling state [14,16] around a defect or impurity or in a self-trapped state? Estle [1], against, cites the lack of line broadening the novel temperature dependence and spectra, but Haller [17] favours tunnelling and conclusions must be based on a detailed model.

(d) Are transient states involved? Suggestions include excited states like $[\tilde{\mu}^+ e]$ or $[\mu^+ \tilde{e}]$, bound exciton states $[\mu^+ e\,eh]$ [14] and localisation in minima which are not the lowest [18].

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