The energetics of hydrogen in aluminium calculated from first principles

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A De Vita and M J Gillan†

Physics Department, University of Keele, Keele, Staffordshire ST5 5BG, UK

Abstract. The energetics and electronic structure of an isolated hydrogen impurity in bulk aluminium and in the aluminium–vacancy system are studied by *ab initio* methods. The calculations are based on the local density approximation and the supercell approach, with a norm-conserving pseudopotential for aluminium and the bare Coloumb potential for hydrogen. The relaxed electronic ground state is determined by the conjugate-gradients technique. Results are presented for the heat of solution, the relative energies of different interstitial sites, the energy profile for migration of hydrogen between sites, and the trapping energy and equilibrium location of hydrogen bound to a vacancy. The heat of solution is close to the measured value, and the tetrahedral site is energetically favoured over the octahedral site, as indicated by experiment, though the energy difference between the sites is comparable with the uncertainties in the calculations. Hydrogen is found to be bound to the vacancy in a strongly off-centre position, with a binding energy that is somewhat smaller than the experimental value.

1. Introduction

The problem of providing an adequate theory of the energetics of hydrogen in metals has attracted enormous interest over many years (see e.g. Friedel 1952, Puska and Nieminen 1984, Daw and Baskes 1984, Fukai and Sugimoto 1985, Nørskov and Besenbacher 1987). There are both scientific and technological reasons for this. Since hydrogen is the simplest possible impurity, there is a strong scientific incentive to obtain a thorough fundamental understanding of its properties. From the technological viewpoint, there are two important reasons for studying hydrogen in metals. The first has to do with the harmful effects of dissolved hydrogen, such as embrittlement and fatigue; the second arises from the continuing interest in metal hydrides as energy storage systems. The motivation for the present work is scientific. Recent advances in techniques for treating the total energy of materials from first principles have made possible the reliable and accurate calculation of impurity and defect energies (Srivastava and Weaire 1987, Ihm 1988, Payne *et al* 1991, Gillan 1991, De Vita and Gillan 1991). The purpose of this paper is to report new calculations on hydrogen in aluminium based on these new techniques.

The case of hydrogen in aluminium has attracted strong interest, because aluminium is one of the most important simple metals; the literature already contains many papers on the energetics of this system (Popovic *et al* 1976, Larsen and Nørskov

† Also at: InTec, Harwell Laboratory, AEA Technology, Oxfordshire OX11 0RA, UK.

1979, Manninen and Nieminen 1979, Kahn *et al* 1980, Estreicher and Meier 1983, Solt *et al* 1983, Craig 1983). However, all previous calculations have been based on uncontrolled approximations, which were necessary at the time, but which can now be avoided. Our aim in the present work is to avoid, as far as possible, the approximations made in earlier studies.

Most of the previous work has taken as its starting point the proton in jellium (Popovic *et al* 1976, Almbladh *et al* 1976, Nørskov 1979, Larsen and Nørskov 1979, Nørskov and Lang 1980, Puska *et al* 1981, Estreicher and Meier 1983). This starting point is certainly relevant, because of the nearly-free-electron nature of aluminium, but it does not by itself provide a useful description of the energetics, because it ignores the interaction of the proton and its surrounding electron screening cloud with the ionic cores. The simplest way of accounting for this describes the electron–core interaction by a pseudopotential, whose effect is treated by first-order perturbation theory. The early work of Larsen and Nørskov (1979) showed that this interaction produces a large correction, which is crucial to an understanding of the energetics. This approach was studied in detail by Estreicher and Meier (1983), who found that the results depended considerably on the pseudopotential employed, and concluded that first-order perturbation theory is not sufficiently reliable. An alternative approach, pioneered by Almbladh *et al* (1976) and used by several other workers (Manninen and Nieminen 1979, Kahn *et al* 1980, Perrot and Rasolt 1981), avoided perturbation theory, but at the expense of making a spherical approximation for the potential due to the ions. Most of the earlier work ignored relaxation of the lattice surrounding the hydrogen, the belief being that the effect of this on the energy would be negligible. The fact that this is not the case was appreciated by Perrot and Rasolt (1981) and Solt *et al* (1983), and will be confirmed in the present work.

The work we report here avoids the most serious approximations made in previous treatments of the aluminium–hydrogen system. Our key remaining approximation is the widely employed local density approximation for exchange and correlation, which we believe produces only small errors for this system. The valence–core interaction for aluminium is represented by a fully non-local *ab initio* pseudopotential. The calculations employ periodic boundary conditions, so that we treat a periodic array of protons in the aluminium crystal. In principle, the electronic interaction of the screened protons could produce effects which for present purposes are spurious, but we shall provide evidence that these effects are small for the sizes of repeating cell we employ. All our calculations fully include the relaxation of all ions in the system. We shall present results for the heat of solution, the relative energies of different interstitial sites, the migration energy for hydrogen diffusion and the binding energy and the location of the stable site for hydrogen bound to a vacancy.

2. Methods

Since the methods used in this work have been described in detail in previous papers (Gillan 1989, De Vita and Gillan 1991), it will be sufficient here to summarize the main points. We also describe in this section a perturbative correction which we have introduced to treat the high-wavevector components of the Coulombic electron–proton interaction.

The work is based on the local density approximation for electronic exchange and correlation, the exchange–correlation energy as a function of electron density being

that of Perdew and Zunger (1981). Valence electrons only are treated. The electron–core interaction for aluminium is described by a pseudopotential having the non-local Kleinman–Bylander form (Kleinman and Bylander 1982). This includes s- and p-non-locality, and is based on the *ab initio* semilocal pseudopotential of Bachelet *et al* (1982). Full details of the pseudopotential are given in our earlier paper (De Vita and Gillan 1991), where we show that it accurately reproduces the equilibrium lattice parameter and bulk modulus of aluminium and gives a satisfactory account of the energetics of the vacancy and the self-interstitial systems. The electron–proton interaction is taken to be the bare Coulomb interaction.

The electron orbitals are expanded in plane waves up to a cut-off energy E'_{cut} which we normally take to be 13 Hartrees. This large cut-off is needed to deal with the singular Coulomb potential of the proton and the associated cusp in the wavefunctions, as discussed in more detail below. Brillouin-zone sampling is performed using the Monkhorst–Pack scheme (Monkhorst and Pack 1976), and a finite-temperature Fermi surface smoothing technique is employed to increase integration efficiency. The quantity minimized corresponds formally to the total free energy in the fixed volume of the unit cell, at a fictitious temperature corresponding to a small fraction of the Fermi energy of the free-electron gas of the same density (Gillan 1989). An accurate approximation to the ground-state energy is then obtained as the mean of the energy and the free energy (Gillan 1989, De Vita and Gillan 1991).

Simultaneous relaxation of the electron orbitals to self-consistency and of the ionic positions to equilibrium is accomplished by the conjugate gradients technique, which is described in detail in earlier papers (Gillan 1989, De Vita and Gillan 1991). We have noted before that this is a reliable and robust method for locating the minimum energy configuration of defect and impurity systems, but since we have not reported before on the efficiency of the minimization procedure, it will be helpful to illustrate here the typical course of such a calculation. We show in figure 1 the total free energy as a function of iteration number for the system of 27 aluminium atoms with hydrogen at the tetrahedral site. Here, a single iteration consists of a full electronic orbital displacement plus the ionic relaxation in the updated electronic charge distribution. In the initial configuration, all ions are on perfect lattice sites, with the initial valence density taken to be a superposition of atomic densities. The initial orbital wavefunctions are those obtained by diagonalization of the Kohn–Sham Hamiltonian constructed from this approximate density, the diagonalization being performed with a small plane-wave cut-off energy, which was 1.5 Hartree in the case illustrated. For the purposes of the present work, one needs to ensure convergence of the total energy to within about 10^{-3} Hartree. As the figure shows, the conjugate gradients procedure achieves this in less than 30 iterations for the maximum cell size adopted in the present calculations, and for a geometry in which lattice relaxation will be seen later to be energetically decisive.

Finally, we describe briefly a perturbation correction we have applied in order to account for the omission of plane waves above the cut-off E'_{cut}. The main purpose of this is to correct for our inaccurate treatment of the cusp in the wavefunctions at the proton. It should be noted that this correction is expected to be rather small because of the high primary cut-off we use. In addition, the correction is not expected to affect significantly the relative energies for hydrogen at different positions, since the error is unlikely to depend much on position. However, we shall see later that its effect on the heat of solution is not completely negligible.

The correction is applied once only to the sum of single-particle energies, after
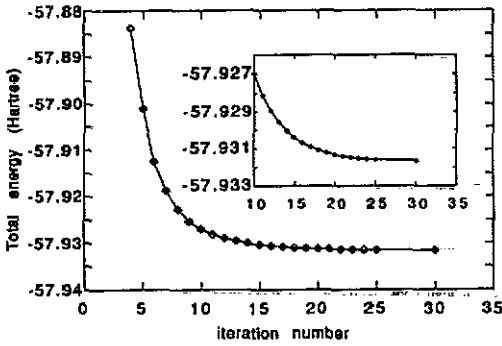
Figure 1. Illustration of the convergence of the total free energy to structurally relaxed self-consistency as a function of iteration number. The results are for hydrogen at the tetrahedral site in a system of 27 aluminium atoms; they show that convergence to better than 10^{-3} Hartree is obtained within 30 iterations.
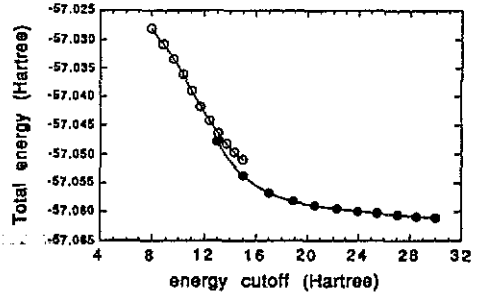
Figure 2. A test of the perturbative correction. The plot shows the fully converged total energy, E_{tot}, for hydrogen at the tetrahedral site in a system of 27 aluminium atoms at a sequence of values of the secondary cut-off energy E''_{cut}. White and black symbols show the results for the primary cut-off energy E'_{cut} set equal to 8 and 13 Hartree respectively.

self-consistency has been achieved, and takes the form of the usual second-order perturbation expression. The matrix elements of the potential in this expression are those connecting plane waves below the cut-off to those above. The correction $\delta\epsilon_{qi}$ to the eigenvalue of orbital i at sampling wavevector q is given by:

$$\delta\epsilon_{qi} = \sum_{G(|G+q|>k_c)} \frac{|\langle\psi_{qi}|V_{KS}|G+q\rangle|^2}{\epsilon_{qi} - \frac{1}{2}|G+q|^2}. \tag{1}$$

Here, ψ_{qi} and ϵ_{qi} are the unperturbed eigenfunction and eigenvalue of orbital i at sampling vector q, $|k\rangle$ is the plane-wave state at wavevector k, and V_{KS} is the Kohn–Sham potential operator. The sum only goes over plane waves whose wavevector $G+q$ is greater than the cut-off wavevector k_c, which is related to the primary energy cut-off E'_{cut} by $E'_{cut} = \frac{1}{2}k_c^2$; it extends up to a secondary energy cut-off E''_{cut}. The correction to the total energy is then taken to be:

$$\delta E = \sum_q w_q \sum_i f_{qi}\delta\epsilon_{qi} \tag{2}$$

where w_q is the sampling weight at wavevector q and f_{qi} is the occupation number of orbital i at this wavevector.

We have made checks to verify that this perturbative correction achieves what is required. A word is needed here about what we demand of the correction. Suppose we have made a fully self-consistent calculation using a primary energy cut-off E'_{cut}, and we have applied the perturbative correction using a secondary cut-off E''_{cut}, thus

obtaining the estimate E_{tot} for the total energy. If the correction is effective, then the estimate E_{tot} should not vary if E'_{cut} is varied with E''_{cut} held fixed. In fact, it is useful to examine E_{tot} as a function of E''_{cut} for each given E'_{cut}: it is straightforward to calculate the correction for a sequence of values of E''_{cut}. According to what we have said, plots of E_{tot} against E''_{cut} for different values of E'_{cut} should coincide. As an illustration of this, we show in figure 2 results for the total energy obtained for hydrogen at the tetrahedral site in a system of 27 aluminium atoms. The figure shows E_{tot} including the perturbative correction as a function of E''_{cut} for $E'_{cut} = 8$ and 13 Hartree. The two curves coincide to within about 2×10^{-3} Hartree. The figure also shows that the correction lowers the energy by some 15×10^{-3} Hartree, which is not negligible when one considers the heat of solution. It is worth noting that the perturbative correction used here is similar to the one applied by van de Walle *et al* (1989) in their recent calculations on hydrogen in silicon.

3. Results

3.1. A preliminary test

In order to provide a check on our methods, we have used them to calculate the embedding energy of a hydrogen atom in jellium. This is a rather powerful check, because the problem of embedding hydrogen in jellium bears a strong resemblance to that of embedding hydrogen in a metal. On the other hand, the embedding energy of hydrogen in jellium over a range of densities was well established some years ago through much simpler calculations which made use of the spherical symmetry of the system (Almbladh *et al* 1976, Zaremba *et al* 1977, Nørskov 1979). The idea is, then, that by comparing the results obtained for this system using our present techniques with the established results we are subjecting our techniques to a fairly stringent test.

In making this check, we use exactly the same periodic boundary conditions, Fermi surface smoothing and Brillouin-zone sampling as in the calculations on aluminium reported below, but of course with the bare Coulomb potential of the proton as the only external potential acting on the electrons. The embedding energy is the difference of two energies. The first is the ground-state energy of the periodically repeated system of $N + 1$ electrons and one proton in volume Ω; the second is the energy of the system N electrons in the same volume plus the energy of an isolated hydrogen atom, the latter being taken to have its exact value of -0.5 Hartree. The electron density N/Ω is given the value appropriate to bulk aluminium, namely 0.0269 au.

Two quantities govern the accuracy of these calculations: the plane-wave cut-off energy and the number of sampling points. The dependence of the total energy of the embedded hydrogen system on cut-off energy is almost identical to that displayed in figure 2, though of course with a shift in the energy zero. The results quoted below were obtained with a secondary cut-off of at least 30 Hartree, which appears to be enough to ensure convergence of the total energy to within 2.5×10^{-3} Hartree.

In order to correct for any incompleteness of Brillouin-zone sampling, we apply the 'jellium correction' employed in our previous work on defects in aluminium (De Vita and Gillan 1991). The idea is that for calculations of the present kind, the sampling error is similar to the error that would be incurred in a calculation on pure jellium. We therefore use the given periodic boundary conditions, Fermi surface smoothing and number of sampling points to calculate the total energy of jellium

for the number of electrons of interest, and subtract from this the exact value. This error is the jellium correction, which is subtracted from the total energy of the system under study.

Table 1. Embedding energy ΔE of hydrogen in jellium (energy of embedded hydrogen system minus energy of jellium plus isolated hydrogen). The difference between the uncorrected and corrected ΔE is the jellium correction (see text). The reference values of ΔE are those of a: Almbladh *et al* (1976); b: Zaremba *et al* (1977); c: Nørskov (1979).

	16-atom	27-atom
ΔE (eV) uncorrected	1.36	1.57
ΔE (eV) corrected	1.51	1.50
ΔE (eV) reference	1.30[a,b]	1.51[c]

We have performed our test calculations on the hydrogen embedding energy in jellium for numbers of electrons corresponding to 16 and 27 aluminium atoms in the appropriate volume. The temperature T controlling the Fermi smoothing was 0.1 of the Fermi kinetic energy in jellium, and two Monkhorst–Pack sampling points in each irreducible wedge were used. Our results for the hydrogen embedding energy in jellium are reported in table 1, both with and without the jellium correction (but including in both cases the perturbative correction). The jellium correction applied to the perturbatively corrected results gives our best calculated values; these are compared with the standard literature results, which come from calculations performed in spherical symmetry. The close agreement indicates that the heat of solution reported later should be subject to a technical error of at worst about 0.2 eV.

The literature values for the embedding energy refer, of course, to the embedding energy of hydrogen at infinite dilution. Our conclusion is therefore valid only if we can assume that the interaction between periodically repeated hydrogens can be neglected. We believe this neglect is justified by the extremely efficient and highly localized electronic screening of the proton. This is confirmed by the close agreement between the results for different cell sizes.

3.2. Stability of interstitial sites and heat of solution

There are two possible interstitial sites for hydrogen in aluminium: the octahedral site and the tetrahedral site. It is clear from previous work (Manninen and Nieminen 1979, Kahn *et al* 1980, Perrot and Rasolt 1981, Estreicher and Meier 1983, Solt *et al* 1983) that the energy difference between the two sites is rather small.

We have calculated the ground-state energies for hydrogen at these two sites, both with and without lattice relaxation, for systems containing 16 and 27 aluminium atoms. It is convenient to present each energy as an embedding energy of the type discussed in section 3.1, i.e. as the change of energy on going from perfect bulk aluminium plus an isolated hydrogen atom to the system containing the same number of aluminium atoms, with the hydrogen at an interstitial site. As before, we apply the jellium correction; this does not affect relaxation energies or the relative energies of sites, though it does affect the heat of solution.

The calculated energies are presented in table 2. A number of important points are noteworthy. Firstly, the difference between the relaxed energies of the two sites is

Table 2. Results of calculations on hydrogen at tetrahedral (tet) and octahedral (oct) sites for periodic systems having 16 and 27 aluminium atoms. The embedding energy ΔE (energy of fully relaxed system with hydrogen minus energy of perfect crystal plus isolated hydrogen atom) is given without and with the perturbative correction (see text). The energy of solution E_{sol} is obtained by adding to ΔE the experimental dissociation energy per atom of the H_2 molecule (2.24 eV). Also shown are the relaxation energy (energy of unrelaxed minus energy of relaxed systems) and the relaxational displacement of nearest-neighbour aluminium atoms.

	16-atom		27-atom	
	tet	oct	tet	oct
ΔE (eV) no pert.	−1.08	−0.96	−1.11	−1.07
ΔE (eV) with pert.	−1.29	−1.15	−1.30	−1.24
E_{sol} (eV)	0.95	—	0.94	—
Relax. energy (eV)	0.36	0.04	0.32	0.05
Relax. displ. (Å)	0.12	0.03	0.12	0.04

small: 0.14 eV in the 16-atom system, and 0.06 eV in the 27-atom system. Secondly, in both systems the relaxed tetrahedral site is more stable. Thirdly, lattice relaxation plays an important role in determining the relative stability of the sites. The reason for this is that the relaxation energy for the tetrahedral site is over 0.3 eV, while the octahedral relaxation energy is only a few hundredths of an eV. We comment further on these points in section 4, where we also discuss possible reasons for the variation of the calculated energies with system size. In order to obtain the heat of solution, we have to add the dissociation energy per atom E_D of the hydrogen molecule to the most negative embedding energy, namely that for the tetrahedral site; since we expect our results for the 27-atom cell to be the most accurate, we take this embedding energy to be −1.30 eV. We could choose to take the value of E_D either from calculation or from experiment; we take the experimental value $E_D = 2.24$ eV (Beutler 1934). The resulting heat of solution is 0.94 eV, which should be compared with the experimental values of 0.83 eV (Ransley and Neufeld 1948) and 0.66 eV (von Eichenauer 1968). The significance of this agreement will be discussed later.

The form of the electronic screening charge surrounding the proton is of considerable interest. Figure 3(*a*) shows a contour plot of the valence electron density on the (110) plane passing through hydrogen at the tetrahedral site. The extremely localized nature of the screening charge, already known from previous calculations on hydrogen in jellium, is immediately clear. It is also clear that the presence of the screened proton induces only very small changes in the electron distribution around neighbouring aluminium atoms. This fact is even clearer if we calculate the screening charge distribution itself, by which we mean the difference of charge distribution between the system with hydrogen and the perfect aluminium crystal. In order to make this difference meaningful, we need to calculate it for the ionically *unrelaxed* system, because otherwise the displacements of the aluminium atoms would themselves contribute substantially to the charge difference. The screening charge distribution calculated in this way for hydrogen at the tetrahedral site in the 27-atom system is shown in figure 3(*b*). This picture shows two remarkable features. Firstly, the distribution has almost complete spherical symmetry, with hardly any disturbance due to the aluminium lattice, except in the region of the nearest neighbours. This provides a justification for the common assumption that the charge distribution can be approxi-
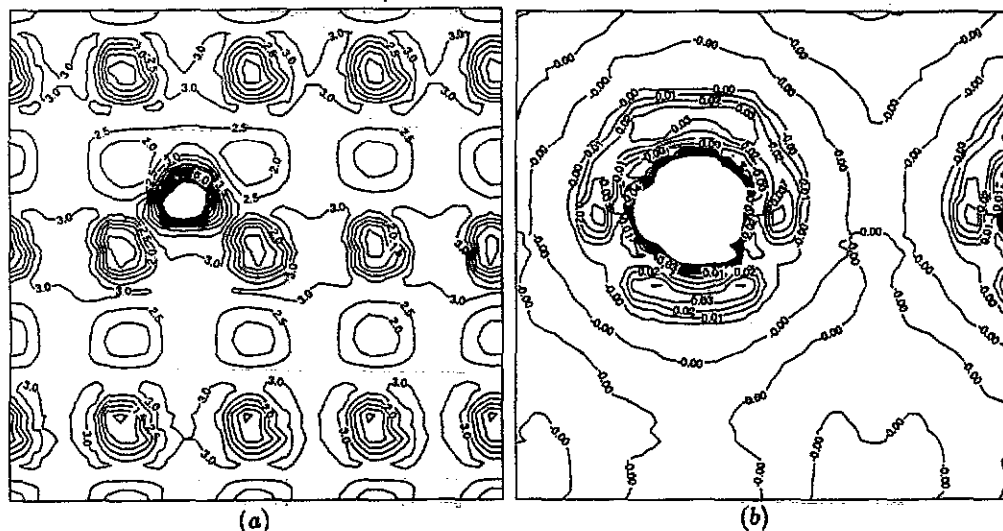
Figure 3. (*a*) Contour plot of the electron density on the (110) plane passing through hydrogen at the tetrahedral site in a system of 27 aluminium atoms. Values marked on contours indicate the electron number density in units of 10^{-2} electrons per Bohr radius cubed (in these units the average electron density is 2.7). (*b*) The screening electron density (see text) corresponding to (*a*); units of electron density as in (*a*).

mately represented as a rigid superposition of the proton screening charge in jellium and the charge distribution of the host metal (Larsen and Nørskov 1979, Estreicher and Meier 1983). Secondly, one sees clearly the extremely efficient localization of the screening charge. We estimate that in the region midway between the periodically repeated protons the magnitude of the screening charge density is less than 4×10^{-3} times the bulk density. This very small value provides further support for the neglect of electronic interactions between the protons, which we assume in interpreting our results for the energetics.

3.3. Hydrogen migration energy

The migration energy for diffusion is the energy barrier that the hydrogen must surmount as it diffuses between interstitial sites. Since previous work, as well as physical intuition, indicates that the lowest barrier is obtained if we move the hydrogen along the (111) direction between the tetrahedral and octahedral sites, we have calculated the energy profile along this path.

In calculating the barrier height, the relaxation of the metal atoms must be included: we require the lowest barrier that would be found if we were to search over all paths in configuration space connecting the relaxed tetrahedral and octahedral configurations. In order to identify the barrier, we have performed calculations in which the system is relaxed to full equilibrium with the proton fixed at a series of positions on the line joining a tetrahedral site to a neighbouring octahedral site, while the centroid of the system of host atoms is also held fixed. (Some constraint must be imposed on the host system during relaxation, since otherwise it would move bodily until the proton arrived back at an interstitial site. The choice of host centroid seems to be the most economic and least arbitrary; it is crucial to note that, although this choice affects the detailed form of the energy profile, it does not affect the barrier height.)
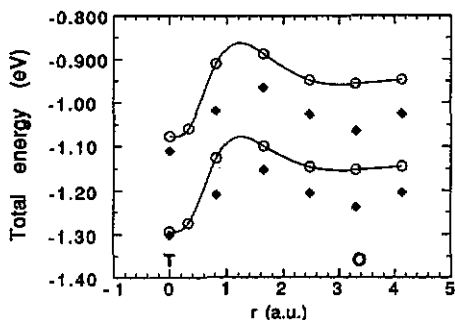
Figure 4. Profile of the total energy of the fully relaxed system as a function of proton position along the straight line in the (111) direction between tetrahedral (T) and octahedral (O) sites. White circles and black diamonds show results for the 16-site and 27-site systems respectively. The upper and lower sets of symbols show respectively results obtained without and with the perturbative correction.
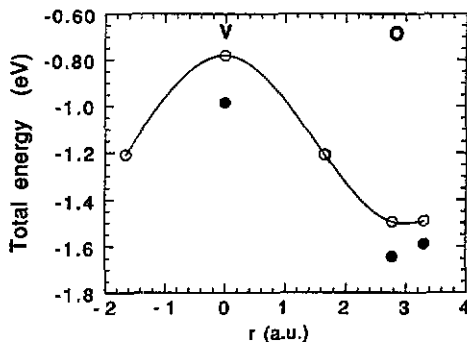
Figure 5. Profile of the total energy of the fully relaxed hydrogen-vacancy system as a function of proton position on the straight line in the (111) direction between the centre of the vacancy (V) and a neighbouring tetrahedral site (T). White and black circles show respectively the results obtained for the 16-atom and 27-atom systems.

The calculated energy profiles for the fully relaxed systems of 16 and 27 host atoms are displayed in figure 4. The energies at the interstitial sites themselves are those reported in section 3.2. We mentioned above that the perturbative correction has little effect on relative energies within the same system. This is illustrated in the figure, which shows the migration profiles obtained without and with the correction. The two profiles differ only by an essentially constant energy shift. The migration energy, which is the energy difference between the barrier top and the most stable interstitial site, is 0.20 eV for the 16-atom system and 0.15 eV for the 27-atom system. The correct experimental value of the migration energy is unfortunately not clear, as we shall discuss later.

3.4. Binding energy of hydrogen to a vacancy

When considering the binding of hydrogen to a vacancy, two questions are important. Firstly, we need to know the configuration of the hydrogen–vacancy system that gives the lowest energy. Secondly, we require the binding energy: the difference between the energy of this configuration and the energy of the same system when the hydrogen and the vacancy are well separated.

In seeking the equilibrium configuration, we have not made a complete search. We report here the fully relaxed energies only for configurations in which the proton lies on a series of positions on the line in the (111) direction joining the centre of the vacancy to a neighbouring tetrahedral site. As in the calculations on the migration energy, the total energy is minimised with the centroid of the host system held fixed. The calculated energies for the 16- and 27-atom systems are displayed in figure 5.

We note that the hydrogen is not stable at the centre of the vacancy; this confirms what has already been found in earlier, more approximate calculations (Larsen and Nørskov 1979). The most stable configuration we find has the proton displaced by only a small amount from the tetrahedral site, the energy being lower than that of the vacancy–centre configuration by about 0.7 eV.

The binding energy is obtained as the difference between two embedding energies, the first being the energy for embedding the hydrogen in the relaxed vacancy system with the hydrogen at the minimum-energy configuration discussed above, and the second being the fully relaxed energy for embedding a hydrogen atom at the tetrahedral site in the perfect host system. The calculated binding energies for the 16- and 27-site systems are 0.19 and 0.34 eV. Our conclusion is thus that hydrogen is bound to a vacancy, though we note that the binding energy is considerably lower than the values obtained in early calculations (Popovic and Stott 1974, Larsen and Nørskov 1979), which were of order 1 eV. The experimental value of the binding energy is 0.52 eV (Myers *et al* 1989).
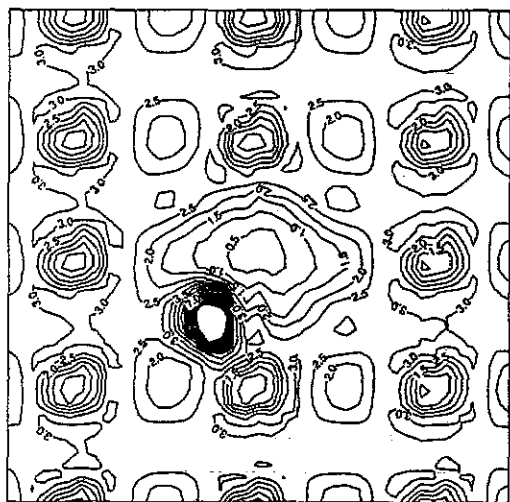

Figure 6. Contour plot of the electron density in the vacancy–hydrogen system. The density is shown on the (110) plane passing through the vacancy centre and the proton at its most stable position. Values marked on contours indicate the electron number density in units 10^{-2} electrons per Bohr radius cubed (in these units the average electron density is 2.7).

Figure 6 shows the valence electron density in the (110) plane passing through the stable position of the hydrogen and the centre of the vacancy.

4. Discussion

We discuss in this section how our calculated results relate to previous theoretical work and to experimental measurements. Before doing this, it will be useful to comment on the technical aspects of our calculations.

Apart from the assumptions involved in the local-density approximation, the main sources of inaccuracy in the calculations are the pseudopotential approximation, the Fermi-energy smoothing, the plane-wave cut-off, the size of the repeating cell, and the Brillouin-zone sampling. The use of non-local pseudopotentials and Fermi-energy smoothing in the representation of the metal host in the calculation has recently been discussed in a study of the vacancy defect in aluminium (De Vita and Gillan 1991),

where LDA-APW results were available for comparison. Given the large cut-off energy we have used, and our perturbation correction for plane waves beyond the cut-off, we believe that inaccuracies due to the cut-off do not have a significant influence on our results. The question of system size is more problematic, since we do see differences between the results for our 16-atom and 27-atom calculations which are significant; for example, the embedding energies at the octahedral site differ by as much as 0.1 eV, which is not fully satisfactory. The possible reasons for such differences are of three kinds: firstly, there may be significant *electronic* interaction between the impurities; secondly, lattice relaxation may be influenced by system size; thirdly, Brillouin-zone sampling errors will be affected by the size of the system. We have shown that electronic interaction between the impurities is probably negligible, and we certainly do not expect it to affect energy differences. Lattice relaxation effects cannot be ruled out, but we note from table 2 that the calculated relaxation energies are very little affected by the size of the system. The most likely culprit therefore seems to be insufficient fineness of the sampling. We are, of course, already working close to the limits of what is currently feasible, but it would clearly be desirable in future work to extend these calculations to larger cell sizes with finer sampling. A useful discussion of cell size effects in metal-hydrogen calculations has recently been given by Koudou *et al* (1990).

We now turn to a comparison with earlier theoretical and experimental results. We note first that our calculated heat of solution of 0.94 eV is in reasonable agreement with the experimental values of 0.83 eV (Ransley and Neufeld 1948) and 0.66 eV (von Eichenauer 1968). We have shown that our techniques, when applied to the embedding of hydrogen in jellium, successfully reproduce the known embedding energy.

We find that the fully relaxed tetrahedral and octahedral interstitial configurations are very close in energy, the tetrahedral configuration being lower by 0.06 eV according to the results for our largest cell. This is in general accord with previous calculations (Manninen and Nieminen 1979, Kahn *et al* 1980, Perrot and Rasolt 1981, Estreicher and Meier 1983, Solt *et al* 1983), which all find very similar energies for the two configurations. Our most significant result here concerns the important role played by lattice relaxation. Our calculated relaxation energy for the tetrahedral site is 0.32 eV, which is much greater than the value of 0.05 eV for the octahedral site. This is not unexpected, since the distance between the proton and its nearest neighbours is smaller in the tetrahedral than in the octahedral configuration by a factor $\sqrt{3/2}$. Our conclusion is that lattice relaxation is one of the main physical factors determining the relative stability of the sites. The evidence from ion-channelling experiments favours the tetrahedral site, though it has been suggested that the octahedral site may be occupied under certain conditions (Bugeat and Ligeon 1979, Ligeon *et al* 1986, Myers *et al* 1989). It seems clear from both theory and experiment, then, that the relative stability of tetrahedral and octahedral sites is a fairly subtle matter, about which one cannot yet be completely confident.

The migration energy we find (0.20 eV and 0.15 eV for the 16- and 27-site systems) is lower than the value of typically 0.5 eV obtained in some earlier calculations (e.g. Kahn *et al* 1980). One reason for this is certainly that our calculations are the first in which the lattice relaxation accompanying migration is fully included. Again, the experimental situation is not very clear. The most reliable measurements appear to be those of Papp and Kovacs-Csetenyi (1981) and of Hashimoto and Kino (1983), both performed at temperatures above about 600 K, which give values of 0.40 and 0.61 eV respectively. However, Hashimoto and Kino find that the activation energy

decreases strongly when the temperature is reduced to about 300 K. Their suggestion is that intrinsic diffusion of hydrogen is observed at low temperatures, but that at high temperatures most of the hydrogen is bound to vacancies. Circumstantial evidence for a rather low migration energy of hydrogen in aluminium comes from a consideration of the diffusion coefficient of positive muons. It is well known that muons diffuse much more rapidly in aluminium than in copper over a wide range of temperature, to the extent that muon spin relaxation is unobservable in aluminium unless the muons are trapped at impurities, though it is easily observable in copper (Seeger 1978, Kehr *et al* 1982, Hartmann *et al* 1988). This suggests that the energy barriers in aluminium must be lower than in copper. But the activation energy for hydrogen in copper is well established to be 0.40 eV (Katz *et al* 1971, Perkins and Begeal 1972). It therefore seems to us unlikely that the activation energy in aluminium could be greater than this. Our conclusion is that, while our calculated value is somewhat low compared with the available data, it is not necessarily in conflict with experiment.

On the question of the binding of hydrogen to vacancies, we find, in agreement with earlier work (Larsen and Nørskov 1979), that the stable size for bound hydrogen is strongly displaced from the vacancy centre. As we have stressed, our search over hydrogen positions is limited to the line along the (111) direction between the centre of the vacancy and a neighbouring tetrahedral site. Along this direction, the minimum of energy occurs at a point very near the tetrahedral site, but displaced slightly towards the vacancy, in qualitative agreement with the results of channeling experiments (Myers *et al* 1989). The restriction of our calculations to a particular search line was, of course, dictated only by limitations of computer resources, but we recognise that a more extended search would be desirable. Our hydrogen-vacancy binding energy for the 27-site cell is 0.34 eV. This is somewhat smaller than the experimental value of 0.52 eV (Myers *et al* 1989). We note that early calculations gave much larger values in the region of 1 eV (Larsen and Nørskov 1979).

In conclusion, we believe that the methods used in this work have much to offer for the study of hydrogen impurities in metals. We are currently attempting to extend the calculations to treat the energetics of hydrogen in niobium. The use of pseudopotential methods for transition metals raises new problems, because of the strong d-wave component of the pseudopotential and the strongly localized nature of the d-orbitals. However, these are problems that can be overcome, as is clear from the recent pseudopotential calculations of Wang *et al* (1989) on hydrogen in palladium.

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