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Equilibrium configuration of bond-centered H^0 in GaAs

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The equilibrium structure of neutral interstitial hydrogen near the bond-centered site in GaAs is calculated at the *ab initio* Hartree-Fock level in the cluster $HGa_4As_4H_{18}$ using a split-valence basis set and *ab initio* pseudopotentials for the core orbitals. The calculated spin densities and various other properties agree well with the muon-spin-rotation and level-crossing resonance-spectroscopy measurements.

I. INTRODUCTION

In the past few years, hydrogen has been one of the most studied impurities in semiconductors for a variety of reasons (for a recent review, see Ref. 1). Hydrogen directly contributes to the removal or creation of many defects: It saturates dangling bonds,[2,3] passivates[1,4,5] shallow acceptors and donors, and can even activate[6,7] electrically inactive defects. Hydrogen is also known to play more indirect roles such as enhancing[8,9] the diffusion of interstitial O in Si. Further, H also exists as an interstitial in a number of semiconductors. Most of the experimental information comes not from hydrogen itself, but from a light pseudoisotope of H, muonium, via muon-spin rotation (μSR), muon or pion channeling, and level-crossing-resonance- (LCR) spectroscopy measurements (recent reviews of the expermental techniques and results can be found in Refs. 10 and 11): Various paramagnetic and diamagnetic forms of muonium have been seen in diamond, Si, Ge, SiC, GaP, and GaAs. The "diamagnetic" forms of muonium (which could be either a bare μ^+ or Mu^-) usually coexist with at least one (but often both) paramagnetic species, which are labeled "normal" and "anomalous" muonium (Mu and Mu*). Mu is characterized by an isotropic hyperfine interaction, and is usually thought[12–23] to be at or near (one of) the tetrahedral interstitial site(s) in the diamond (zinc-blende) lattice. On the other hand Mu* has trigonal symmetry, and corresponds to the interstitial at (or near) the center of a covalent bond: the evidence for this location stems from experimental data[24–26] in Si, GaP, and GaAs, as well as from a variety of theoretical results in diamond,[14] Si,[17–21] and more recently, zinc-blende BN and BP.[22] In the cases of diamond[27] and Si,[28] there is experimental evidence that Mu* is more stable than Mu. A recent successful EPR observation[25] of H^0 in Si has shown that hydrogen behaves in an essentially identical manner to muonium, except for small differences associated with the larger zero-point motion of the muon than of the proton.

Most of the theoretical studies of interstitial hydrogen in semiconductors have been done on two group-IV hosts: diamond[11–14] and silicon.[17–21] Recently, zinc-blende BN and BP have been included,[22] and calculations involving Ge clusters[23] have been completed. In the present work we report similar calculations in the case of GaAs. Our results are consistent with the emerging picture for neutral interstitial hydrogen in semiconductors, confirm the interpretation of experimental data[26,29] for Mu* in GaAs, and the chemical structure obtained is similar to that[22] of H^0 in *c*-BN and *c*-BP. In Sec. II we discuss our calculation, and in Sec. III we compare our results to the experimental data.

II. THE CALCULATIONS

The host crystal is represented by a cluster containing two host-atom shells around the center of a Ga—As bond: $Ga_4As_4H_{18}$. The two central atoms are not connected to any of the surface saturators. Since experimental evidence is that the interactions involving Mu* in GaAs are highly localized[26,29] [almost all of the unpaired spin density can be accounted for by including the impurity and its nearest neighbors (NN's)], this cluster probably provides a reasonable representation of the situation under study. The next-larger[22] cluster symmetric around the bond-centered site and containing an equal number of group-III and -V atoms is $Ga_{22}As_{22}H_{42}$, which is too large for the type of calculations being presented here. In the perfect cluster, the Ga and As atoms are at their crystallographic sites ($a_L = 5.650$ Å). Each second-shell host atom is saturated with three[22] H atoms in such a way that all the host atoms are tetrahedrally coordinated. The host-saturator bond lengths were optimized as discussed in Ref. 30. At equilibrium, we find $d(\text{Ga—H}) = 1.590$ Å and $d(\text{As—H}) = 1.468$ Å.

The calculations[31,32] were performed at the *ab initio* Hartree-Fock (HF) level with restricted (closed-shell) wave functions for the perfect cluster, and unrestricted (open-shell) wave functions when a hydrogenlike impurity is included. In order to remove the core orbitals from the calculation, we used *ab initio* pseudopotentials,[33] which are corrected for relativistic effects. We verified that pseudopotential and all-electron calculations closely agree, irrespective of the code used.[31,32] All the calculations were performed using double-ζ basis sets for the valence orbitals. The geometry optimizations around the impurity have been performed assuming C_{3v} symmetry, and only the first NN's around the impurity and the impurity itself have been displaced. We expect this to be a reasonable approximation; as in all cases where also second-NN's have been allowed to relax,[15,17,22] the net effect was a lowering of the total energy by a few tenths of an eV, without significant changes in the equilibrium structure of the defect.

III. RESULTS AND DISCUSSION

There is a unique minimum of the total energy for neutral interstitial hydrogen along a relaxed GaAs bond. If the first NN's to the H^0 are relaxed and the position of H^0 optimized, this minimum is 1.39 eV above the configuration where atomic H is far away from the unperturbed cluster. This number gives an upper limit to the solubility of H^0 in GaAs.

In the optimized geometry, the Ga—As bond relaxes by 34.5% to accommodate the hydrogen interstitial. This is consistent with the experimentally estimated[26] 32(7)%. In our calculations, Ga moves by 0.526 Å, As by 0.319 Å, and the interstitial H is slightly displaced from the middle of the bond towards the Ga atom. In the final configuration, H is 1.677 Å from Ga [d(Ga—H)=1.67 Å in gallium monohydride] and 1.614 Å from As (1.519 Å in arsene). It should be noted that although the net magnitude of the relaxation is consistent with the one predicted in Ref. 26, we find that Ga is displaced significantly more than As, in contrast to the estimate[26] based on s-orbital spin polarization from calculations on the GeH_3 radical. We found no evidence that a configuration with H slightly off the trigonal axis could be more stable, or that a second (metastable) site exists elsewhere along the axis. The average curvature of the energy for displacements of H along the bond is 8.5 and 0.9 eV/Å^2 perpendicular to it.

Concerning the chemical structure, a qualitative picture can be drawn from the following arguments. In the Ga—H—As configuration, H may either form a stronger bond with Ga with the odd electron in a nonbonding orbital on As, or vice versa. Which of these two configurations is realized depends on the relative strengths of the Ga—H versus As—H bonds, and on the stability of the unpaired electron in an antibonding orbital on As versus on Ga. In the present case, the As—H bond is slightly stronger than the Ga—H bond (the dissociation energies[34] are 3.6 and 2.8 eV, respectively), but the odd electron is more stable on As. Thus the two possible configurations compete more than in other III-V compounds where the two bond strengths are essentially comparable (or even favor[22] the group-III atom), while the electronic affinity of the group-V atom dominates. This leads to clear-cut situations where the group-III atom dominates the interaction (see, e.g., the discussion of Ref. 22), while most of the unpaired spin density is localized on the group-V atom. In the case of bond-centered H^0 in GaAs, the spin density is shared by the two host atoms along the bond, slightly more on As than on Ga for the reasons discussed above. The calculated spin density along the bond is shown in Fig. 1.

Experimentally, the hyperfine frequencies of the anomalous muonium state in GaAs can be determined very accurately.[26] The component of the tensor along the ⟨111⟩ axis $A_\parallel$ is 218.54(3) MHz, and the perpendicular component $A_\perp$ is 87.87(5) MHz. To compare with the present calculations, we prefer to consider the contact and dipolar frequencies

$$\nu_C=(A_\parallel+2A_\perp)/3 \quad\text{and}\quad \nu_D=(A_\parallel-A_\perp)/3 .$$

The experimental values become $\nu_c=131.4$ MHz and $\nu_D=43.6$ MHz. The calculated value for ν_C at the equilibrium site for the impurity is 20 MHz. In view of the fact that zero-point-motion effects are neglected and that our basis set contains no polarization functions, the abso-

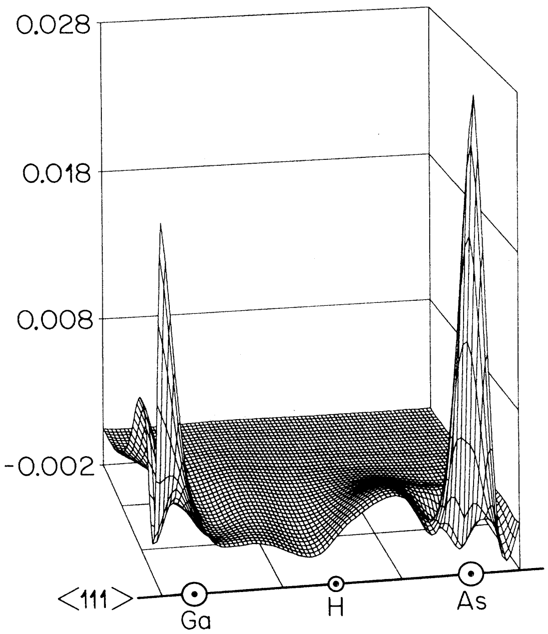

FIG. 1. Unpaired spin density for hydrogen (or muonium) near the center of a covalent bond in GaAs. The Fermi-contact density at the impurity is very small, and more of the odd electron is located near the group-V than near the group-III atom (see text). The spin density is in atomic units. The plot was obtained from a calculation using the cluster $HGa_4As_4H_{18}$, with a split-valence basis set for the valence orbitals and *ab initio* pseudopotentials for the cores, except the central Ga and As atoms, which are treated at the all-electron level.

lute deviation from the experimental result is very small. Further, in contrast to the corresponding[23] values in diamond, Si, and Ge, the value of ν_C is positive. The dipolar frequency ν_D can, in principle, be obtained from our calculated spin density. However, it depends much more on the amount of lattice relaxation than on the details of the spin distribution:[35] were all of the unpaired electron on the Ga (As) atom, ν_D would be 53 (60) MHz in our equilibrium geometry. Both numbers are very close to the experimental value. Further, the experimental estimate of the amount of unpaired electron density localized on Ga and As is 38% and 45%, respectively. As can be seen in Fig. 1, our spin distribution is very similar. Another quantity which can be compared to experimental data is the ratio of the populations of the atomic p to s orbitals. For the Ga and As atoms nearest the impurity, we obtain 3.8 and 50 (4.0 and 23 experimentally[26]).

In conclusion, our calculations predict with good accuracy all of the experimental findings for anomalous muonium in GaAs. The only qualitative disagreement is related to the amount of relaxation of the Ga and As atoms from their undisturbed substitutional sites. However, the experimental estimates for these displacements have been obtained in a very indirect manner.

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