

Electronic structure of hydrogen-based impurity complexes in crystalline germanium

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Hydrogen in association with other impurities (C, Si, or O) in pure crystalline germanium forms electrically active, shallow carrier centers. The charge states in the vicinity of these centers are studied in a Bethe-cluster approach with a minimal basis. The important electron-electron repulsion in the neighborhood of the H site is included. The observed charge states, both for acceptors (C and Si) and donors (O) are associated with double occupation of the H-site orbital. Physical mechanisms favoring double occupancy are discussed. Results are compatible with the systematics of the observed results.

Hydrogen, in conjunction with certain other impurities, makes electrically active shallow level centers in ultrapure germanium.¹⁻⁵ In particular [H,C] and [H,Si] are shallow acceptors and [H,O] is a shallow donor. They all exhibit full tetrahedral symmetry but cannot be explained by the standard theory of shallow substitutional centers: Dynamic behavior of the proton is required. A major issue to be explained is that, while atomic H alone in crystalline Ge is believed to be a rapidly diffusing neutral interstitial,^{6,7} when trapped in the vicinity of the heavier impurity it attracts an extra charge, either positive or negative, and becomes a shallow electrically active, dynamic complex. The presence or absence of this extra charge is fundamentally related to the electron-electron Coulomb repulsion⁸ at the hydrogen site and to the "spatial extent" of its 1s orbital. In general, the Coulomb repulsion tends to favor a single-electron occupancy and a neutral state. We point out that in H⁻ the binding energy of the second electron is only 0.7 eV, implying a large Coulomb repulsion, ~ 1 Ry. We expect that the effective repulsion operative in these complexes would be roughly equally important.

It should be remarked that a doubly occupied hydrogen 1s orbital in [H,C] or [H,Si] yields directly a shallow-acceptor complex. A doubly occupied hydrogen 1s orbital⁹ in substitutional [H,O], given the two extra electrons provided by the atomic oxygen, yields a positively, singly charged complex center and hence a shallow donor.

We studied these effects by means of a simplified but realistic model, an infinite system consisting of the following: (a) a central cluster cage formed by 9 germanium atoms and one substitutional impurity atom [see Fig. 1(a)]; (b) a single hydrogen atom which is located within the 10-atom cage; (c) 16 tetrahedrally coordinated Bethe lattices (Cayley trees)¹⁰ which saturate all the sp^3 bonds of the 10 cage atoms.

Included are (i) 4 tetrahedrally distributed sp^3 orbitals for each of the 10 cage atoms and for each atom in the 16 Cayley trees; (ii) a single 1s state for the hydrogen atom. These orbitals are assumed to form an orthonormal set.

The Hamiltonian, which is of the tight-binding type, includes the following: (1) diagonal orbital energies for the hydrogen 1s and the impurity sp^3 orbitals, measured from the germanium sp^3 diagonal orbital energy; (2) intra-atomic interorbital energies for the germanium atoms; (3) intra-atomic interorbital energies for the substitutional atom; (4) interatomic "hopping" energies between all possible orbitals

of nearest-neighbor germanium atom pairs [see Fig. 1(b)]; (5) "hopping" energies between the substitutional impurity sp^3 orbitals and all germanium nearest-neighbor orbitals; (6) "hopping" energies between the hydrogen 1s orbital and all the sp^3 orbitals of the 10-atom cage; (7) a Hubbard-type electron-electron Coulomb repulsion U between two electrons with opposite spin in the hydrogen 1s orbital only.

The contribution (7) is the only two-body term and is treated in the Hartree-Fock approximation.⁸ The choice of tight-binding parameters was guided by previous calculations for the Ge lattice,^{11,12} atomic term values and their interpre-

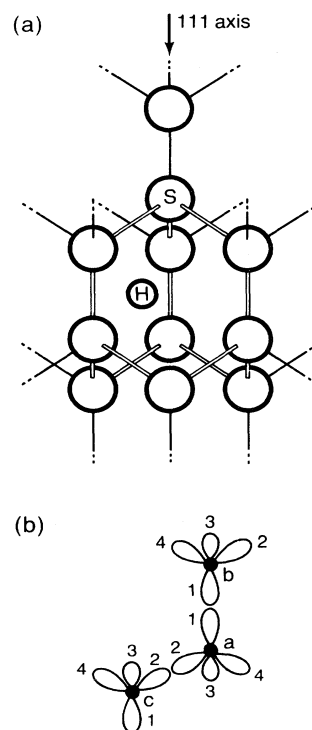


FIG. 1. Projection of the tetrahedral cage onto the $(\bar{1}\bar{1}\bar{1})$ plane. Double lines connect the atoms of the cage. The substitutional site (S) forms the top of the cage. Single lines and dots indicate how fourfold Bethe lattices are connected to the cage. The hydrogen site (H) is located within the volume of the cage.

tation,¹³ atomic calculations;¹⁴⁻¹⁶ and other calculations for hydrogen in semiconductors.^{7,17} In particular, for [H,C] and [H,O], we chose the following: the center of gravity of the sp^3 orbitals in carbon to be 4 eV below the germanium value; the center of gravity of the oxygen orbitals to be 8 eV below those of germanium; the intrasite, interorbital matrix elements to be (-2) eV for Ge and C and (-4) eV for O; the intersite hopping matrix elements for Ge-Ge bonds to be those of Ref. 11; and the intersite hopping matrix elements for C-Ge and O-Ge bonds to be equal to each other and to a fraction 0.75 of those of the Ge-Ge bond. The hydrogen-related parameters were estimated mostly from Refs. 7 and 17 and by calculating overlap integrals between the hydrogen 1s orbital and the various Slater sp^3 orbitals.¹⁶ The electron-electron interaction parameter U was also taken to be a function of the position of H in the cage, i.e., a function of the extent of the 1s orbital. It was taken to be $U = 7$ eV at the cage center and $U = 5$ eV for H near the substitutional atom (1.93 a.u.) in the [111] antibonding direction.

The electronic spectrum of the system was obtained self-consistently by means of a Green's function calculation similar to those used to treat magnetic impurities⁸ and/or chemisorbed atoms.^{18,19} The projected density of states on the hydrogen 1s orbital for each spin σ was calculated as a function of the total occupancy $\langle n_{H\bar{\sigma}} \rangle$ of the opposite spin in the same orbital and, by integrating up to a Fermi level determined by the total number of electrons, a system of two equations for $\langle n_{H\uparrow} \rangle$ and $\langle n_{H\downarrow} \rangle$ was obtained. Solutions with $\langle n_{H\uparrow} \rangle = \langle n_{H\downarrow} \rangle$ are nonmagnetic and in our case were always connected with double occupancy of the hydrogen 1s orbital, with extra charge in the neighborhood of the cage and with an electrically active (shallow carrier) complex. Solutions with $\langle n_{H\uparrow} \rangle \neq \langle n_{H\downarrow} \rangle$ correspond to magnetic-moment formation in the vicinity of the hydrogen, and in our case either to a neutral state of the cage and a deep-level impurity complex [H,C] or to an unstable double donor [H,O].

It should be remarked that there were important qualitative differences between the spectrum of our problem and those of Refs. 8, 18, and 19. The most important difference was the semiconductor character of our crystal, with its attendant valence band, energy gap, and conduction band. In addition, there were *two* impurities in our problem: hydrogen and the substitutional C, Si, or O. Localized states may appear in our spectrum in three regions: below the valence band, within the energy gap, and above the conduction band. These localized states can be of several kinds: (1) "atomiclike" in character, originating from the hydrogen 1s orbital or from the substitutional impurity sp^3 orbitals; (2) bonding and antibonding orbitals arising from various diatomic combinations and/or molecular clusters. It was of great importance to determine the character of these localized states, their weight at the hydrogen 1s orbital, and their relative position with respect to the Fermi level. The "residue" of each such state in the density of states projected onto the hydrogen 1s orbital must be included in the self-consistency equations if and only if the localized state for that spin falls below the "effective" Fermi level. It should be noted that, because the Bethe lattice tends to exaggerate the gap by a factor of about 3, all localized states above the top of the Bethe lattice valence band and below the actual valence edge are occupied, i.e., the effective Fer-

mi level is restricted to the region of the actual gap.

A summary of our results follows. With the hydrogen at the center of the cage (distance $R_H = 4.63$ a.u. from substitutional atom) a magnetic solution $\langle n_{H\uparrow} \rangle \neq \langle n_{H\downarrow} \rangle$ was always found, with essentially single occupancy of the hydrogen 1s orbital and a paramagnetic state. For both a Ge-only cage and [H,C], this state was locally neutral and H becomes a very deep donor. For [H,O], which in this configuration must certainly be unstable, the hydrogen was neutral and the oxygen atom, similarly to the chalcogens, behaves as an ordinary double donor. Results for the three cases are shown in Fig. 2. We obtain

$$\langle n_{H\uparrow} \rangle = 0.970, \quad \langle n_{H\downarrow} \rangle = 0.062, \quad \text{for [H,C] ;}$$

$$\langle n_{H\uparrow} \rangle = 0.940, \quad \langle n_{H\downarrow} \rangle = 0.063, \quad \text{for [H,O] ;}$$

$$\langle n_{H\uparrow} \rangle = 0.994, \quad \langle n_{H\downarrow} \rangle = 0.057, \quad \text{for [H] .}$$

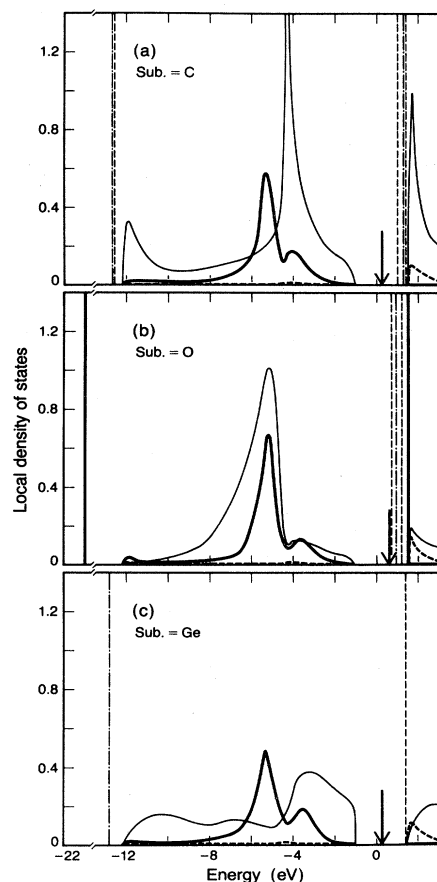


FIG. 2. Local density of states for hydrogen at the cage center ($R_H = 4.63$ a.u. from substitutional atom) and for three different substitutional atoms. Dark solid lines are projections onto the hydrogen site for up spin. Dashed lines are for down spin. Light solid lines are projections onto the four sp^3 orbitals of the substitutional site for spin up. For spin down—not shown—the results are almost identical to spin up. Vertical lines are discrete, localized states: Dot-dashed lines are for spin up, dashed lines for spin down, and solid lines for lines in which both spins practically overlap. Arrow denotes position of the effective Fermi level.

When the hydrogen atom was placed close to the substitutional impurity (distance $R_H = 1.93$ a.u. along the [111] axis in the antibonding direction and towards the cage center) the situation changed drastically. Nonmagnetic solutions are found for [H,C], where $\langle n_{H\uparrow} \rangle = \langle n_{H\downarrow} \rangle = 0.930$, and for [H,O], where $\langle n_{H\uparrow} \rangle = \langle n_{H\downarrow} \rangle = 0.870$. For pure germanium, however, the solution was magnetic: $\langle n_{H\uparrow} \rangle = 0.978$, $\langle n_{H\downarrow} \rangle = 0.182$. This implied that, for hydrogen near a substitutional impurity, [H,C] is a shallow acceptor (singly, negatively charged complex), [H,O] is a shallow donor (singly, positively charged complex), but [H] by itself is still a deep donor (neutral complex). These results are shown in Fig. 3.

The results discussed above lead us to the following conclusions:

(1) As the hydrogen moves away from either a C or an O impurity towards the center of the cage, a crossover between a nonmagnetic and a magnetic solution must appear; the crossover was estimated to be at $R_H = 2.70$ a.u. for [H,C] and at $R_H = 4.25$ a.u. for [H,O].

(2) Hydrogen remained a neutral, magnetic impurity in a large region of the pure germanium cage, in agreement with the fact that H is, in crystalline Ge, a rapidly diffusing neutral interstitial.

(3) The lower value of the site energy at the substitutional site—directly related to the lower atomic numbers of carbon and oxygen as compared to germanium—seems to be paramount in promoting double occupation at the H site and the consequent shallow impurity character.

(4) For a hydrogen 1s orbital energy well in the middle of the germanium valence band—as is known to be the case—there are four factors which tend to promote nonmagnetic solutions of the equations (i.e., double occupancy of the hydrogen orbital). They are (i) lowering of the hydrogen site energy; (ii) a decrease in the value of the electron-electron interaction U ; (iii) a decrease, at constant U , in the hybridization strength between the hydrogen site and the lattice; and (iv) lowering of the orbital energies at the substitutional site.

(5) When hydrogen is located in the neighborhood of a low-atomic-number substitutional impurity, all four effects listed above become operative and, if the overall complex is stable, a shallow center—acceptor for C, donor for O—results.

(6) It should be emphasized that our conclusions should be regarded as preliminary and intended primarily to elucidate mechanisms rather than determine quantitative spectral values. Indeed our results are somewhat sensitive to the specific values of the tight-binding parameters, parameters which in the present context can only be considered approximate. The mechanisms discussed here and their physical origins, however, are internally consistent, very “reasonable,” and explain in a global way the empirical facts of this complicated field.

(7) We have not explicitly calculated spectra for the [H,Si] complex. Experimentally it behaves as a less tightly bound [H,C] system: It is a doubly occupied shallow-acceptor center. The tight-binding parameters of Si and Ge cannot be meaningfully distinguished. In view of the experimental facts and our results for Ge we believe that probably hydrogen in pure Ge is “marginally” neutral, while hy-

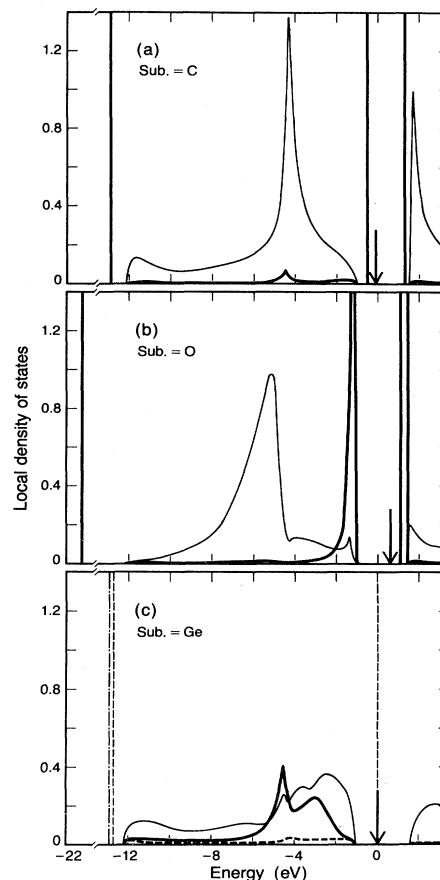


FIG. 3. Local density of states for hydrogen near the substitutional atom ($R_H = 1.93$ a.u. in the antibonding direction, towards the cage center) and for three different substitutional atoms. Symbols are as in Fig. 2. For (a) carbon and (b) oxygen the Hartree-Fock solutions are nonmagnetic; for (c) germanium a magnetic solution is found.

drogen in [H,Si] in germanium is marginally a doubly occupied acceptor. Details of this work and additional results will be reported elsewhere.

(8) Additional physical questions remain unanswered: Why is hydrogen attracted to substitutional C, Si, and O? Is [H,O] really a substitutional impurity complex? What is the mechanism by which it is formed? Is there a [H,S] donor complex in germanium? Can the dynamic character of the proton around the heavier impurity be explained from first principles?

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