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AB-INITIO CLUSTER CALCULATION OF HYPERFINE INTERACTIONS AND TOTAL-ENERGY SURFACES FOR N IN DIAMOND, SILICON AND GERMANIUM

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AB-INITIO CLUSTER CALCULATION OF HYPERFINE INTERACTIONS AND TOTAL-ENERGY SURFACES FOR N IN DIAMOND, SILICON AND GERMANIUM

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ABSTRACT

Using an ab-initio LCAO unrestricted Hartree-Fock cluster model we study the electronic structure of the substitutional N impurity in C, Si and Ge. We find that the stable position for the impurity is off-center in a $\langle\bar{1}\ \bar{1}\ \bar{1}\rangle$ direction in all cases. The results for the hyperfine interactions over the impurity and first neighbors are in fair agreement with experiment.

1 Introduction

The purpose of this work is to investigate the behavior of the N impurity in group IV semiconductors C, Si and Ge. We may thus follow the trends in electronic structure for the system when the environment of the impurity changes from 2sp → 3sp → 4sp. In spite of the large amount of theoretical studies of N in diamond [1,2] and Si [3,4], this is the first calculation of the electronic structure of N in Ge through an "ab-initio" method. From experiment, also, the situation in diamond and Si is well known: electron paramagnetic resonance (EPR) data indicate that in both cases the center is distorted from T_d symmetry, the impurity displaced along a $\langle\bar{1}\ \bar{1}\ \bar{1}\rangle$ direction. We show in this work that an "ab-initio" cluster calculation can describe well the known experimental results; we further predict the behavior of N in Ge, for which we obtain the total-energy surface for movement of the central atoms, together with the magnetic hyperfine interactions.

2 Model

We use 17-atoms clusters consisting of a central atom, a first shell of four nearest-neighbors and a second shell of twelve hydrogen atoms to saturate the dangling bonds. The "perfect" crystals are then simulated by clusters in T_d symmetry: C_5H_{12}, Si_5H_{12} and Ge_5H_{12} A N atom replaces the central atom for study of the impurity systems, that is, clusters NX_4H_{12} , with X=C, Si or Ge.

The electronic structure is obtained using an all-electron "ab-initio" LCAO procedure. The molecular orbital expansion is over the primitive gaussian contracted to some sets, and all one-electron, two-electron and overlap integrals are fully calculated, with no pseudopotential. We have used the basis set proposed by Dunning and Hay [7]: 4s contracted 2s for H; 9s5p contracted 3s,2p for C; and 12s,5p contracted 6s,4p for Si. For Ge we used the "Husinaga-MIDI" basis set [8]. The calculation was performed using program GAMESS [9] in both Roothaan Open-shell Hartree-Fock (ROHF) and unrestricted Hartree-Fock (UHF) schemes.

3 Results and Discussion

The N substitutional impurity, for all 3 cases, introduces an a_1 antibonding state in the gap region and, to higher energies, a t_2 state. The ground state configuration in T_d symmetry is then obtained as $|...a_1^1t_2^0>$ leading to a non-degenerate ground state $^2A_1$; a Jahn-Teller distortion is not bound to occur. Although we find that the systems distort to a C_{3v} symmetry, we will not enter here in the discussion about the reasons for this distortions, if from a chemical rebonding of a pseudo Jahn-Teller effect.

Using the procedure described in the last section we calculated the total-energy for a large number of positions of the central impurity-coupled to displacement of one of the nearest neighbors-in the impurity clusters.

We show in Fig.1 the results of such a calculation for a grid of 68 coupled displacements. We see that N is unstable in T_d symmetry in the three cases, moving to C_{3v} symmetry. We must stress that, in diamond and silicon, if we displace only the atom, keeping the first neighbors fixed, no off-center minimum is found: for this to happen, it is essential that the C (Si) atom is allowed to move in <111> direction away from the impurity. This finding agree with the results of Schultz and Messmer [4] that if the N atom is inside a rigid Si cage, the stable geometry would be tetrahedral.

The atomic displacements we obtain from our calculation of the minima in the energy surfaces are: for the N-atom, in a $\langle\bar{1}\ \bar{1}\ \bar{1}\rangle$ direction away from the T_d substitutional site, 0.23Å in diamond, 0.47Å in Si and 0.49Å in Ge; for the ligand atom on the C_{3v} axis in the <111> direction away from the impurity, 0.36Å in diamond, 0.47Å in Si and 0.48Å in Ge. For these coupled displacements, the gain in (cluster) total energy is 1.01 eV in diamond, 0.72 eV in Si and 0.63 eV in Ge.

We now turn to the analysis of bond-charge and spin distribution. The charge distribution is obtained from the bond-order matrix P_{AB}, for atoms A and B. Using the fact that the molecular orbital ψ_a is built in LCAO form

$\psi_a(\vec{r})=\Sigma_\mu C_{a\mu}\chi_\mu(\vec{r})$ from the atomic orbital χ_μ, the bond-order matrix is built from the orbital population on density matrix $P_{\mu\nu}=\Sigma_a^{occ} C^*_{\mu a} C_{\nu a}$ as $P_{AB}=\Sigma_\mu^A \Sigma_\nu^B P_{\mu\nu}$ where μ is centered at A and ν at B. The spin density over center A is defined as $\langle S\rangle_A=\langle S^\alpha\rangle_A-\langle S^\beta\rangle_A$, where $\langle S^\alpha\rangle_A=\Sigma_{\mu\nu}^A P^\alpha_{\mu\nu}$. We show in Table I the results for the bond order between the ligand and the N impurity P_{LN} and the spin density $\langle S\rangle$ over each distinct center: in T_d symmetry all ligands are equivalent, in C_{3v} we distinguish the ligand lying in the C_{3v} axis (A) from the three other ligands lying in a plane perpendicular to the axis (P).

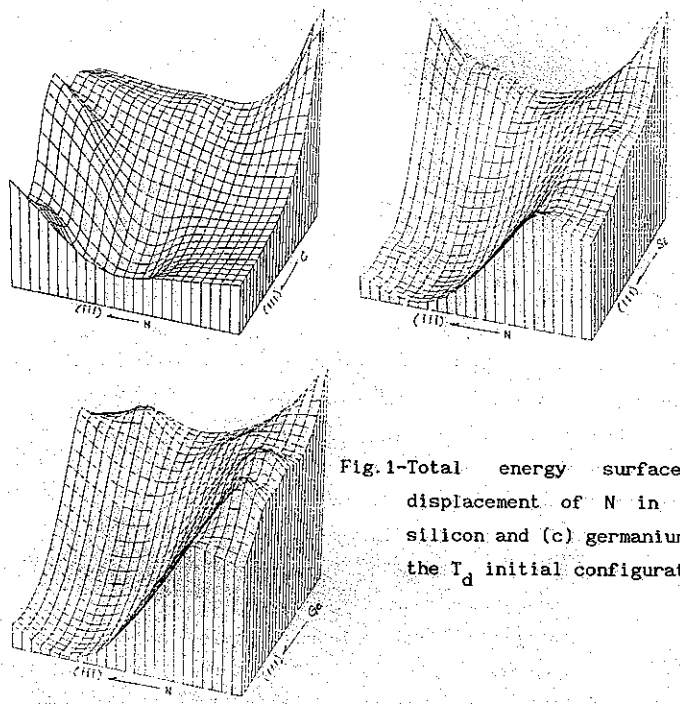

Fig.1-Total energy surface for coupled displacement of N in (a) diamond (b) silicon and (c) germanium. The arrow marks the T_d initial configuration

Table I: Results for bond order P and spin density <S> obtained in this work for the systems C:N, Si:N and Ge:N, in tetrahedral T_d symmetry and in the minimum-energy configuration, of C_{3v} symmetry.

	Substitutional(T_d)			Displaced(C_{3v})				
	$\langle S\rangle_L$	P_{LN}	$\langle S\rangle_N$	$\langle S\rangle_P$	P_{PN}	$\langle S\rangle_N$	P_{AN}	$\langle S\rangle_A$
C	0.3	0.1	0.1	~0.0	0.26	0.08	-0.52	0.12
Si	0.31	0.15	0.4	~0.0	0.29	~0.0	0.01	1.22
Ge	0.49	0.24	0.24	~0.0	0.36	0.01	0.06	1.84

To analyse this results we must consider that the lattice parameter of diamond is very small compared to Si or Ge, and also that the Ge valence orbitals (4s and 4p) are very delocalized compared to the lighter elements. In the T_d geometry the bonds are strenghtened down the column from C to Si to Ge, or, looking from another angle, we have higher overlap population in Ge-N bonds. In C_{3v} symmetry at the minimum-energy configuration we obtain similar trends as in T_d, for the bonds with the three closer ligand neighbors (P_{PN}), with higher overlap population compared to T_d, that is, now we obtain really an sp^2 hybridization. The striking result concerns the bond with the ligand on the axis (P_{AN}): the antibonding character of this bond is very clear for the diamond case, even if for Si and Ge if comes off as non-bonding, with overlap population almost null. The results for spin density indicates a very strong magnetic polarization at the ligand Ge site in the C_{3v} axis, with zero spin density at all other sites.

As said in the introduction, there are EPR [5,6] results for N in Si and Ge which provide detailed pictures of the centers. The usual analysis of experimental data approximates the wave-function ψ_e for the electron in the highest molecular orbital a_1 by a simple LCAO:

$$\psi_e=\Sigma_i \eta_i\,(\alpha_i\chi_{i,s}+\beta_i\chi_{i,p}) \qquad (1)$$

where the sum is over valence s and p orbitals at atoms close to the impurity site. We can compare our theoretical results for the isotropic (A_j) and anisotropic (B_j) terms of the hyperfine interation

$$A_j=\frac{8\pi}{3}\,g_e\,\mu_B\mu_N\left\{\frac{\mu_j}{I_j}\right\}\,|\psi_e(0)|^2 \qquad (2)$$

$$B_j=\frac{4}{3}\,\mu_B\mu_N\left\{\frac{\mu_j}{I_j}\right\}\,\langle r^{-3}_{j,e}\rangle \qquad (3)$$

where μ_j is the nuclear magnetic moment of atom j, I_j is nuclear spin. We can write from equation (1)

$$|\psi_e(0)|^2=|\chi_{j,s}(0)|^2\,\eta_j^2\,\alpha_j^2 \qquad (4)$$

$$\langle r_e^{-3}\rangle=\langle r^{-3}_{j,p}\rangle\,\eta_j^2\,\beta_j^2 \qquad (5)$$

where now $|\chi(0)|^2$ and $\langle r^{-3}_{j,p}\rangle$ are taken from Hartree-Fock atomic calculations and the coefficients come from our results. We present then in Table II a comparison between our values for A_j and B_j, and results from EPR [5,6]. We

may see that we obtain an overall agreement, with the exception of the values for the anisotropic term in Si (which, however, present the observed trend), which is very small and not easy to calculate with a small cluster calculation.

Table II: Isotropic and anisotropic hyperfine terms for N impurity in diamond and Si; all entries in units of $10^{-4}cm^{-4}$, obtained using values for isotopes ^{14}N, ^{13}C and ^{29}Si.

	DIAMOND				SILICON			
	C<111>		N		Si<111>		N	
	A	B	A	B	A	B	A	B
Expt.	68.95	22.17	30.37	3.63	95.7	18.4	13.10	1.00
our	63.7	12.5	16.1	3.9	114.1	5.3	3.7	0.3

There are no available experimental results for Ge:N, hence our results are not included in Table II: A= 12.1 x $10^{-4}cm^{-1}$.

Finally, we find, for the minimum-energy C_{3v} configuration, for all three systems, a level very close to the valence band related to the "lone-pair" N orbital, with strong p-character. This orbital is very localized, with strongest localization for the C:N case. This is another indication that the impurity in this C_{3v} configuration shows sp^2 hybridization.

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