RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 60, NUMBER 12 15 SEPTEMBER 1999-II

Ab initio calculation of hyperfine interactions for the $^5A_2$ excited state of the neutral vacancy in diamond

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(Received 18 May 1999)

We calculate the electronic properties and in particular the hyperfine interactions for the $^5A_2$ excited state of V_C^0 and for the unrelaxed $^4A_2$ ground state of V_C^- in diamond. We find fair agreement with experimental electron paramagnetic resonance data for the hyperfine interactions of both defect states. Our results demonstrate that the local spin density approximation yields reliable magnetization densities, not only for the ground states but also for certain excited states of deep defects. [S0163-1829(99)52936-6]

I. INTRODUCTION

Virtually all modern *ab initio* calculations of the electronic structure for deep defects are based on the local spin density approximation of the density functional theory (LSDA-DFT). In this theory, which is valid for the ground state of a system, the basic quantity is the spatial distribution of the spin density, a quantity that unfortunately cannot be compared directly with experimental data. Hyperfine interaction (hfi) data from electron paramagnetic resonance (EPR) experiments offer some information at least about the magnetization density, which is the difference between the spin-up and spin-down spin densities.

While for almost all defects in semiconductors, EPR spectra can be observed for the ground states only, the $^5A_2$ excited state of the neutral vacancy V_C^0 has been observed in diamond.[1] It is therefore interesting to compare theoretical hfi data from *ab initio* calculations with these data. Of course, the DFT is valid only for the ground state of a many-body system. However, within the LSDA, we may restrict the variational degrees of freedom to eigenstates of the total spin S. Within the $S=2$ subspace, the ground state of V_C^0 is the $^5A_2$ state observed experimentally.

We shall also compare calculated hfi data for the $^4A_2$ state of the V_C^- in the negative charge state with the experimental EPR data.[2] For most charge states of the vacancy, there are low-lying configurations besides the ground state configuration. These give rise to electron correlation effects that are beyond the LSDA and must be dealt with by a configuration interaction treatment.[3–5] Fortunately, for both states investigated in this study, there are no further low-lying configurations in the respective spin and symmetry subspaces.

II. COMPUTATIONAL

We have used the linear muffin-tin orbitals method in the atomic spheres approximation (LMTO-ASA) Green's function method[6] for the calculation of the spin densities. In this method, a perturbed region containing the vacancy and its 28 neighbors is embedded into an otherwise perfect crystal. We used a scissors operator technique to adjust the fundamental band gap to its experimental value of 5.5 eV. Details of the computational method have been published elsewhere.[7]

While the calculation for the $^4A_2$ ground state of the V_C^- is straightforward, the $^5A_2$ excited state of the V_C^0 requires that the $a_{1,\downarrow}$ orbital is left unoccupied, an orbital that gives rise to a valence band resonance. While for localized states in the gap the occupancy can be freely chosen, the hole in a valence band resonance is not well-defined in general.

We show in Fig. 1 the density of states (DOS) distribution change induced by the introduction of the vacancy. Vacancy-induced $a_{1,\uparrow}$ and $a_{1,\downarrow}$ resonance states are reasonably sharp to separate the deep hole state from the continuum DOS, because the DOS of the unperturbed crystal has a very small density of s-like states near the top of the valence band. In our calculations for the $^5A_2$ state of V_C^0, we could therefore leave the upper $a_{1,\downarrow}$ resonance unoccupied in the self-consistent cycle.

In our calculations the effects of lattice relaxations were ignored, which, according to recent theoretical work, are small: Li and Lowther[8] report a 10% inward relaxation, Breuer and Briddon[9] find a 13% outward relaxation, whereas according to Zywietz *et al.*,[10] the outward relaxation is 7.3%.

III. RESULTS AND DISCUSSION

For the unrelaxed vacancies we find stable ground states in many charge states ranging from $2+$ to the $4-$ charge

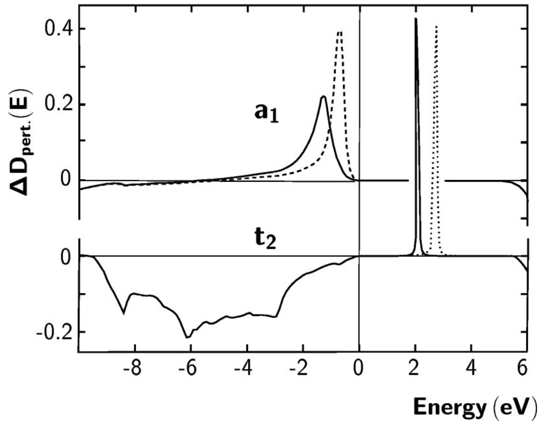

FIG. 1. Induced density of states $\Delta D_{\mathrm{pert}}(E)$ for the negatively charged V_C^- vacancy broken up into a_1 states (upper panel) and t_2 states (lower panel). Full lines mark occupied spin-up states, broken and dotted lines denote occupied and unoccupied spin-down states, respectively.

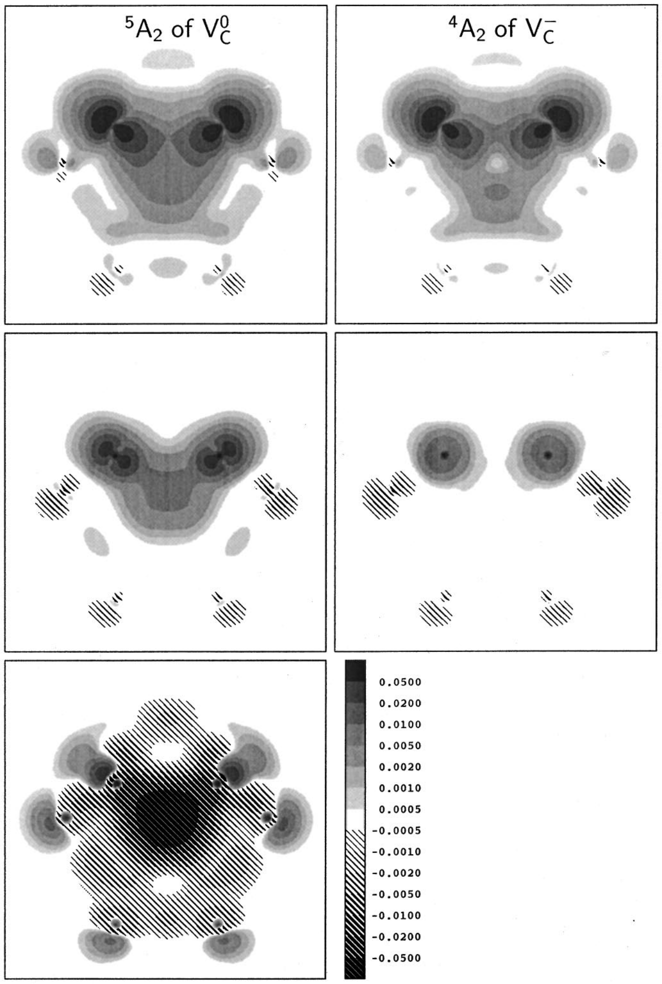

FIG. 2. Contour plot of the total magnetization densities (upper panel), and the magnetization densities induced in the valence bands (middle panel) for the $^5A_2$ excited state of V_C^0 (left), and for the the $^4A_2$ ground state of V_C^- (right), respectively. The contour plot of total induced particle density for the $^5A_2$ excited state of V_C^0 is shown at the bottom.

state. For the negatively charged vacancy V_C^-, the $^4A_2$ ground state can be described as a $a_{1,\uparrow}^1 a_{1,\downarrow}^1 t_{2,\uparrow}^3 t_{2,\downarrow}^0$ configuration of single particle states. The $^4T_1$ excited state of V_C^- is obtained if we change the configuration into $a_{1,\uparrow}^1 a_{1,\downarrow}^0 t_{2,\uparrow}^3 t_{2,\downarrow}^1$. According to our calculation, the total energy of this state is 3.7 eV higher in energy than that of the $^4A_2$ ground state, in reasonable agreement with the 3.149 eV zero phonon line (ZPL) arising from the ND1 defect which is identified with V_C^-.[11] The total energy of this excited state is calculated to be by 0.15 eV higher than that of the $^5A_2$ excited state of the neutral V_C^0 defect with an additional electron in the conduction band. Thus our results are compatible with a spontaneous ionization of the $^4T_1$ state of V_C^- into the $^5A_2$ state of V_C^0. From this state, a transition into the ^1E ground state or into the lower $^1A_1$, $^1T_2$, and $^3A_1$ excited states is highly forbidden. In fact, no other spin quintet can be constructed from a $a_{1,\uparrow} a_{1,\downarrow} t_{2,\uparrow} t_{2,\downarrow}$ basis and, therefore, the $^5A_2$ state of V_C^0 will be long lived.[1]

It is strange that the sharp ZPL transition of ND1 should correspond to the excitation of a valence band resonance into a final state that decays by autoionization. Note, however, that a similar ZPL is observed for the EL2 level in GaAs.[12] Apparently, the width of the LSDA single-particle resonance states does not at all reflect the spread in energy of the corresponding hole states.

It is interesting to compare the spatial distribution of the magnetization densities for the two charge states: In Fig. 2 we display contour plots of the magnetization densities in a (110) plane. These plots differ somewhat from those presented by Bachelet *et al.*,[13] because these authors derive the densities from pseudowave functions that lack the rapid oscillations near the nuclei. For the V_C^- defect, the magnetization density is primarily caused by the gap state, for which the spin-down states are unoccupied. The magnetic moment of the predominantly *p*-like gap state induces a small *s*-like spin polarization of the valence band states at the (1,1,1) ligands. In contrast, there is a strong *negative* spin polarization induced in the valence band states at the (2,2,0) and the $(1,1,\overline{3})$ sites which is predominantly *p*-like. This negative spin polarization is nearly completely balanced by the gap state spin density, such that the resulting total magnetization density at these sites is rather small. The total magnetization density is predominantly due to dangling bonds that transform according to the t_2 irreducible representation. Thus we find no magnetization density at the vacancy center. While most of the magnetic moment is localized at the (1,1,1) ligands, the induced particle density for $^5A_2$ state of V_C^0, which is also shown in Fig. 2, is much more delocalized. This demonstrates that the degree of localization of the magnetization density as inferred from experimental hfi data is not an accurate measure for the localization of the change of the corresponding particle density, which governs the binding of the vacancy.

For the $^5A_2$ excited state of the neutral vacancy, the $a_{1,\downarrow}$ valence band resonance is unoccupied and, therefore, the magnetization density of the valence band states is domi-

TABLE I. Comparison of the calculated ligand hyperfine interaction constants (in MHz) for the unrelaxed excited $^5A_2$ state of V^0 and for the $^4A_2$ state of V^- with experimental data from van Wyk *et al.* (Ref. 1) for the $^5A_2$ excited state of V^0 and from Isoya *et al.* (Ref. 2) for the $^4A_2$ state of V^-.

			(1,1,1) ligand		(2,2,0) ligand			$(1,1,\overline{3})$ ligand		
			a	b	a	b	b'	a	b	b'
$^5A_2$	V^0	this work	88 .0	16.4	−4.7	1.2	0.2	−0.5	0.2	0.1
		exp.	53.73	18.70	6.36	1.2				
$^4A_2$	V^-	this work	126.0	18.1	−3.2	1.2	0.3	−0.4	0.2	0.2
		exp.	101.7	20.0	10.7	1.37	0.085			

nated by the remaining $a_{1,\uparrow}$ spin density. This resonance resembles the a_1 linear combination of the dangling-bond states which is essentially *p*-like at the (1,1,1) ligands. Again we have a near-perfect balance of the magnetization densities at the (2,2,0) and $(1,1,\overline{3})$ sites.

We can check the calculated magnetization densities comparing the resulting hfi data with experimental data in Table I. Here the data are broken up into the isotropic hfi, a, and into the b and b' dipolar contributions. The calculated dipolar contributions agree closely with the experimental data. The somewhat larger deviations for the isotropic hfi with the (1,1,1) ligand could be due to our neglect of lattice relaxations. This could also be the reason for the sign discrepancy of the isotropic hfi with the (2,2,0) ligands. Note, however, that for this ligand, the modulus of the isotropic hfi is very small for either vacancy state. For the (2,2,0) ligand the calculated values for b' are somewhat too large, an artifact that arises from the proximity of the boundary of the perturbed region. Beyond this boundary, the calculated magnetization density must drop to zero, thereby slightly distorting the magnetization density at the ligand.

We thus find that within the LSDA we can satisfactorily describe not only the ${}^4A_2$ ground state of V_C^-, but also the ${}^5A_2$ excited state of V_C^0. This demonstrates that for excited states which differ in total spin from the ground state, the LSDA provides rather accurate magnetization densities. Using the scissor operator technique, we also obtain a reasonable estimate for the ND1 excitation energy of V_C^-.

ACKNOWLEDGMENTS

We would like to thank the Deutsche Forschungsgemeinschaft for partial financial support for this work.

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