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Spin state of vacancies: From magnetic Jahn-Teller distortions to multiplets

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The spin configuration of isoelectronic vacancies surrounded by first-row atoms is studied within density-functional theory (DFT) using the local spin density approximation. Allowing for a symmetry break in the electronic system, a mixed-spin state is found to be lowest in energy. It is accompanied by a magnetization density with reduced symmetry indicating a magnetic Jahn-Teller effect. The DFT results are discussed in terms of many-body wave functions of a quantum-chemical treatment. Examples considered are neutral vacancies in diamond and cubic SiC.

The creation of a monovacancy in tetrahedrally coordinated semiconductors like Si, SiC, and C leaves four dangling bonds at the four nearest neighbors of the missing atom. Provided that the tetrahedral symmetry of the surrounding lattice is preserved, these four dangling hybrids form an *s*-like a_1 state and triply orbitally degenerate t_2 states. For neutral vacancies each type of state can be occupied by two electrons of opposite spin, leading to a degenerate ground state with an electron configuration $a_1^2t_2^2$. Consequently, one expects a symmetry lowering in order to gain energy by lifting this degeneracy. Indeed, this is the case for the neutral vacancy (V_{Si}^0) in silicon and the neutral carbon vacancy (V_{C}^0) in cubic SiC.[1,2] The accompanying strong static Jahn-Teller distortion reduces the spatial symmetry from T_d to D_{2d} by a pairing mechanism and induces a level splitting of t_2 into a single b_2 and a twofold degenerate e state resulting in a configuration $a_1^2b_2^2$.

The situation is completely different for the silicon vacancy (V_{Si}^0) in cubic SiC and the vacancy in diamond (V_{C}^0). A static Jahn-Teller distortion has not been observed. For SiC, calculations within the density-functional theory in local spin density approximation[2–4] (DFT-LSDA) show a stabilization of the vacancy electrons in the high-spin configuration $a_1^2t_2^{\uparrow\uparrow}$. In terms of the defect molecule model[5] this configuration represents a $^3T_1$ multiplet. It has been argued that, due to the relatively large C-C distances of the vacancy neighbors and according to Hund's rule, the local electronic system forms a high-spin state $S=1$ in order to gain energy rather by exchange interaction than by overlap of the C dangling bonds. This explanation is unsatisfactory, however, since in the $^3T_1$ configuration the ground state remains degenerate. Furthermore, the $^3T_1$ ground state of V_{Si}^0, which should be observable by electron paramagnetic resonance, has not been observed by experiment so far.[6] The situation is similiar for the V_{C}^0 defect in diamond. This vacancy also conserves the tetrahedral symmetry. As a consequence, within the defect molecule model the resulting electronic configuration $a_1^2t_2^2$ gives rise to the multiplets ^1E, $^1A_1$, $^3T_1$, and $^1T_2$ of the T_d point-group symmetry.[7] DFT-LSDA calculations can, however, hardly describe differences between multiplets of different symmetry or mixing with $a_1^{2-m}t_2^{n+m}$ excited configurations. A rigorous description of multiplets requires symmetry-adapted exchange-correlation functionals, which are not available so far.[8] Therefore, it is assumed that the LSDA will always predict the multiplet $^3T_1$ as the ground state in the absence of lattice distortion. The best known signature of the V_{C}^0 defect in diamond is the optical band GR1.[9] It is believed to be associated with a transition from the ^1E ground state into a $^1T_2$ excited state. Therefore, V_{C}^0 should be a zero-spin defect and, hence, nonparamagnetic. Until now there is no evidence for the existence of the V_{C}^0 vacancy in the triplet ground state from magnetic resonance measurements.[6,7,9] In the case of the neutral vacancy V_{Si}^0 in cubic SiC such experimental indications are also missing.[10]

Calculations including configuration interaction have recently predicted that the ground state of V_{Si}^0 in cubic SiC should be a singlet (^1E) and not a triplet ($^3T_1$) state.[11] However, with four carbon atoms the clusters used in the calculations were too small to give a definite answer. Also, in earlier studies within the defect molecule model, ^1E rather than $^3T_1$ was determined to be the ground state of the isolated vacancy in diamond[5] and SiC.[12] These findings suggest that exchange-correlation effects beyond the conventional local density treatment might be important for neutral vacancies in SiC and C, which do not undergo a static Jahn-Teller distortion. We believe that this behavior is more general in the case of defects. Other vacancies formed by small atoms in tetrahedral surroundings and occupied by four electrons are further candidates. Examples could be the positively charged cation vacancies V_X^+ in group-III nitrides XN ($X=$B, Al, Ga, and In) or in InP.

In the present paper we carefully study the mutual influence of spin and orbital effects on the spatial symmetry and the total spin of the ground state of neutral vacancies. We use a self-consistent pseudopotential method in the framework of the density-functional theory to calculate the total energies of supercells containing a vacancy. The electron-electron interaction is described within the local spin density approximation. For comparison, calculations are also performed within the local density approximation (LDA). Explicitly, the Perdew-Zunger parametrization[13] of the quantum Monte Carlo results of Ceperley and Alder[14] is used. In order to avoid errors due to frozen cores, nonlinear core corrections to the exchange-correlation energy[15] are included. In the spin-polarized case the correlation energy for arbitrary polar-

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TABLE I. Energy balance for neutral vacancies in diamond and cubic SiC in the triplet and mixed-spin states. The total energy gain is given with respect to the DFT-LDA (GGA) value for the relaxed T_d situation. In addition to the values obtained with a $2\times2\times2$ mesh, the Γ-point results are given in parentheses. All energies are in eV.

	Method	ΔE_{tot}		ΔE_X		ΔE_C	
		Triplet	Mixed	Triplet	Mixed	Triplet	Mixed
V_C^0 in C	LSDA	-0.25	-0.27	-0.76	-1.01	0.15	0.19
		(-0.33)	(-0.36)	(-0.70)	(-0.93)	(0.15)	(0.19)
	GGA	-0.34	-0.40	-0.84	-1.25	0.16	0.23
		(-0.41)	(-0.49)	(-0.79)	(-1.15)	(0.16)	(0.22)
V_{Si}^0 in SiC	LSDA	-0.18	-0.21	-0.66	-1.07	0.12	0.18
		(-0.24)	(-0.29)	(-0.58)	(-0.92)	(0.12)	(0.18)
	GGA	-0.25	-0.35	-0.75	-1.42	0.13	0.23
		(-0.32)	(-0.43)	(-0.66)	(-1.25)	(0.13)	(0.22)

ization is determined by using the same interpolation as for the exchange energy.[16] In addition, we apply the generalized gradient approximation[17] (GGA) to account for the inhomogeneity of the electronic system. Non-norm-conserving Vanderbilt pseudopotentials characterize the electron-ion interaction.[18] We use extremely soft pseudopotentials, which are carefully tested to reproduce the results of calculations with harder potentials for C and SiC.[19] The electron eigenfunctions are expanded in terms of plane waves up to an energy cutoff of 13.2 Ry for SiC and 20 Ry for C. Actually the Vienna *ab initio* simulation package (VASP)[20] is used. The monovacancies are modeled using 216-atom supercells of fictitious simple-cubic crystals. The $\mathbf{k}$-space sampling is performed using the Γ point and a $2\times2\times2$ special-point mesh according to Monkhorst and Pack.[21]

Within the DFT-LDA calculations a T_d symmetry-conserving outward breathing relaxation of 7.1% of the bond length for V_C^0 in C and 9.2% for V_{Si}^0 in SiC is observed.[2,4] In order to investigate the spin influence, the atomic configuration is kept fixed at the resulting positions (T_d symmetry) and DFT-LSDA/GGA calculations are performed, i.e., the total energy is minimized with respect to the spin densities. A high-spin triplet state ($S=1$) is identified as the ground state.[3,4] In both approximations, LSDA and GGA, the systems gain energy mainly due to the exchange interaction as demonstrated in Table I. We have verified that the inclusion of spin polarization does not change the ionic configuration and, hence, the total energy differences ΔE_{tot} given in Table I.

In terms of quantum chemistry and configuration interaction the DFT-LSDA (and also DFT-GGA) possesses a disadvantage. Keeping the T_d symmetry, only averaged configurations with respect to the combination of t_2 orbitals are considered and no excited configurations are taken into account. Therefore, no further spin effects beyond the described exchange-correlation interaction can be obtained. Within the framework of the symmetry restriction it is impossible to achieve a magnetization density of the ground state different from the one discussed above.

To model more than this averaged configuration with spin $S=1$ and to lift the remaining degeneracy, we introduce additional degrees of freedom by allowing the single-electron wave functions to transform according to the irreducible representations of a point group with fewer symmetry operations than T_d. This idea has been tested by keeping the atoms neighboring the vacancy fixed in their relaxed positions of T_d symmetry, but starting with a magnetization density $m(\mathbf{x})=n_\uparrow(\mathbf{x})-n_\downarrow(\mathbf{x})$ that exhibits a reduced symmetry D_{2d}'. The prime indicates a double-valued group representation, i.e., we incorporate spin inversion as an additional symmetry operation. The point group D_{2d}' consists of operations that arrange the four nearest-neighbor atoms in pairs of equivalent ones but, in contrast to T_d and D_{2d}, these two pairs are connected only by operations that simultaneously invert the spin polarization. Consequently, the electrons gain the possibility of occupying single-particle states that are entirely localized at one pair of the four neighboring atoms. The symmetry lowering is accompanied by a splitting of the degenerate t_2 states, the lowest one occupied with two electrons of opposite spins. However, the resulting configuration does not necessarily describe a singlet state ($S=0$). Due to the different localization of the spin-up and spin-down electrons occupying the former t_2 and a_1 levels, the system exhibits a finite magnetization density $m(\mathbf{x})$. The space integral over $m(\mathbf{x})$ vanishes. This means that the quantum number M_S of the total spin projection is zero. The lowered symmetry D_{2d}' influences only the magnetization density $m(\mathbf{x})$, whereas the ionic configuration and the electron density $n(\mathbf{x})$ still transform according to the T_d point-group symmetry. Therefore, we call this effect, giving an energy gain by symmetry lowering, the magnetic Jahn-Teller effect, in analogy with the structural Jahn-Teller effect. Indeed, within the reduced symmetry D_{2d}' we find a new ground state with a total energy lower than that of the high-spin state (cf. Table I).

The resulting spin distribution shows the spatial separation into spin-up and spin-down electrons described above, as can be seen in Fig. 1 (upper panel) for the highest occupied single-electron vacancy states. Surprisingly, such a spatial localization happens also for the a_1-related electrons, as indicated in Fig. 1 (lower panel). The two spinors for the t_2-derived (a_1-derived) electrons in Fig. 1 (upper panel) [Fig. 1 (lower panel)] belong to the same energy level. The spatial part of the spin-down wave function is located at one pair of the vacancy neighbors. That of the spin-up wave function is located at the opposite pair of atoms. Moreover, the delocalized crystal electrons also tend to accumulate at one or the other pair of atoms depending on their spin pro-

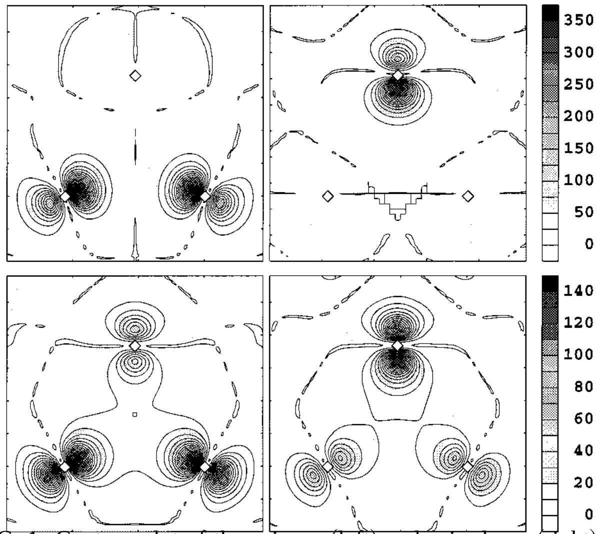

FIG. 1. Contour plot of the spin-up (left) and spin-down (right) wave function square of the mixed-spin state. A (111) plane is shown containing three nearest-neighbor carbon atoms (indicated by diamonds) of the silicon vacancy in SiC. The upper (lower) panel shows the t_2-(a_1) derived states.

jection. The states in the left and right parts of Fig. 1 are connected by a spin rotation and a space rotation around a cubic axis by 180°. This is just one element of the double group D'_{2d}.

Despite the T_d point-group symmetry of the atomic cores the total energy gain resulting for the mixed-spin (but $M_S=0$) electronic configuration with D'_{2d} symmetry is slightly larger than that of the high-spin configuration, as can be seen in Table I. This result is corroborated by the inclusion of generalized gradient corrections. Consequently, the DFT ground state of the neutral vacancy with carbon neighbors in cubic SiC or diamond is a mixed-spin state, not a pure triplet state.[3,4] While the formation of both the high-spin ($S=1, M_S=\pm1$) and the mixed-spin ($M_S=0$) states in the LSDA (and spin-polarized GGA) is clearly exchange driven, the explanation of the smaller energy differences between the two different spin states with a nonvanishing magnetization density is not obvious. In a naive picture one would expect that in the mixed-spin configuration plotted in Fig. 1 the exchange interaction would be remarkably diminished, since the two electrons in the t_2-derived spinors possess opposite spins. The same happens in the a_1-derived electron system. However, vacancy electrons and crystal electrons with the same spin projection are localized at one pair of atoms and interact with each other, i.e., in the LSDA (GGA) the increase of the attractive exchange-correlation interaction in the mixed-spin case with respect to the $S=1$ case is a consequence of the different spatial localization of the single-particle spins.

In terms of DFT,[16] the energy gain for the mixed-spin state is mainly a consequence of the significant magnetization density and, hence, a corresponding enhancement of the exchange-correlation interaction, although the space integral of $m(\mathbf{x})$ vanishes. However, the local sign of the magnetization density is less important for the energy gain. The space integral of $|m(\mathbf{x})|$ gives a value of about 2.7, which is larger than the value of 2.0 in the $S=1$ case. The main contribution (1.7) is due to the t_2-derived states, whereas the other contributions from the a_1-related states (0.7) and from the delocalized valence states (0.3) are smaller. In principle, with the characterized spatial charge and spin configurations of the vacancy electrons we model features of a configuration interaction in the inhomogeneous system even in the framework of the LSDA or GGA.

One can attempt to interpret the LSDA (GGA) results in terms of the quantum chemistry. Unfortunately, one cannot treat all electrons of the system, e.g., the 860 valence electrons in a 216-atom supercell, including the configuration interaction. For the purpose of discussion one can use the defect molecule model,[5,12] i.e., one considers the four vacancy electrons only. The corresponding four-electron wave function can be represented by a single Slater determinant constructed with the one-electron spinors shown in Fig. 1. However, this determinant can be decomposed into four-electron states of different symmetries. The reason is that in general DFT gives rise not to pure multiplets but to many-body states of mixed symmetry and, hence, mixed total spin.[8] In contrast to the quantum-chemical calculations,[5,12] one usually obtains a weighted sum of different multiplet energies. Consequently, the energy of the true ground state with pure symmetry is expected to be even lower than the value given in Table I for the mixed state. This fact can be illustrated using only the most important t_2-derived two-electron subsystem. The corresponding single Slater determinant decomposes into a ^1E ($S=0$, $M_S=0$) state and a $^3T_1$ ($S=1$, $M_S=0$) state with the same weights. The ^1E state is given by the combination $(t_y^{\uparrow}t_y^{\downarrow}-t_x^{\uparrow}t_x^{\downarrow})$ of the single-particle t_2 orbitals and the two-particle singlet spin function. The $^3T_1$ state corresponds to the product of $(t_x^{\uparrow}t_y^{\downarrow}-t_y^{\uparrow}t_x^{\downarrow})$ and the triplet spin function for $M_S=0$. The total energy of the single-determinantal $^3T_1$ state is given by the energy of the high-spin state in Table I. Consequently, the total energies of the mixed state and of the high-spin state in Table I can be combined to obtain the energy of the ^1E state according to Ref. 8. The total energy resulting for ^1E is found to be slightly lower than that of the mixed state. For V_{C}^0 the state splitting between ^1E and $^3T_1$ amounts to 0.04 eV (LSDA) or 0.12 eV (GGA). Experimentally a splitting of 0.04–0.2 eV has been found.[22] This model study indicates ^1E as the ''true'' ground state of the system. However, despite the good agreement with experiment such considerations need not give a final answer concerning the ground state. The use of Kohn-Sham orbitals for the construction of determinants is somewhat dangerous, because the only meaningful quantities in DFT-LSDA are the densities, not the Kohn-Sham orbitals. Moreover, the restriction to a subsystem of electrons is questionable. We find that the interaction of all electrons is important. For instance, the interaction of the defect electrons and the electrons in the extended crystal states is non-negligible. Exchange and correlation of electrons in both subsystems influence the symmetry and the energy of the ''true'' ground state of the total system, the defect in a crystal. On the other hand, the DFT-LSDA/GGA does not give a final answer concerning the symmetry of the many-body state with the lowest energy. One ends up with the single-particle variational quantities $n(\mathbf{x})$ and $m(\mathbf{x})$ only. Unfortunately, there is no direct relation between these quantities and the many-electron wave function of the ground state and, hence, also none between DFT and the defect molecule model.

In summary, we have characterized isolated neutral vacancies in diamond and cubic SiC using DFT in the LSDA or spin-polarized GGA. Within the limitations of the local spin density approximation we made maximum use of the variation of the initial electron density and initial magnetization density. This influences in particular the four-electron system in the t_2- and a_1-derived localized vacancy states. It seems that a part of the configuration interaction in this four-electron system can be modeled by assuming different symmetries of the magnetization density. For the T_d symmetry the single-determinantal high-spin triplet state is favored. On the other hand, the mixed-spin ground state of the vacancies considered becomes slightly lower in energy, allowing a symmetry break to D'_{2d} in the electronic configuration. Within the DFT this state with the lowest energy is related to a significant magnetization density. However, since DFT cannot describe pure multiplets with multideterminantal wave functions, the experimental findings may differ from such a prediction. Therefore, within the defect molecule model we have shown a way to extract a ground state with pure symmetry from the DFT-LSDA/GGA results.

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[1] G.D. Watkins, in *Deep Centers in Semiconductors*, edited by S.T. Pantelides (Gordon and Breach, New York, 1986), p. 147.

[2] A. Zywietz, J. Furthmüller, and F. Bechstedt, Phys. Status Solidi B **210**, 13 (1998).

[3] L. Torpo, R.M. Nieminen, K.E. Laasonen, and S. Pöykkö, Appl. Phys. Lett. **74**, 221 (1999).

[4] A. Zywietz, J. Furthmüller, and F. Bechstedt, Phys. Rev. B **59**, 15 166 (1999).

[5] C.A. Coulson and M.J. Kearsley, Proc. R. Soc. London, Ser. A **241**, 433 (1957).

[6] H. Itoh, A. Kawasuso, T. Oshima, M. Yoshikawa, I. Nashiyama, S. Tanigawa, S. Misawa, H. Okumura, and S. Yoshida, Phys. Status Solidi A **162**, 173 (1997).

[7] J.A. van Wyk, O.D. Tucker, M.E. Newton, J.M. Baker, G.S. Woods, and P. Spear, Phys. Rev. B **52**, 12 657 (1995).

[8] U. von Barth, Phys. Rev. A **20**, 1693 (1979).

[9] G. Davies, S.C. Lawson, A.T. Collins, A. Mainwood, and S.J. Sharp, Phys. Rev. B **46**, 13 157 (1992).

[10] N.T. Son, E. Sörman, W.M. Chen, C. Hallin, O. Kordina, B. Monemar, E. Janzen, and J.L. Lindstrom, Phys. Rev. B **55**, 2863 (1997).

[11] P. Deák, J. Miró, A. Gali, L. Udvardi, and H. Overhof, Appl. Phys. Lett. **75**, 2103 (1999).

[12] F.P. Larkins and A.M. Stoneham, J. Phys. C **3**, L112 (1970).

[13] J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[14] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[15] S.G. Louie, S. Froyen, and M.L. Cohen, Phys. Rev. B **26**, 1738 (1982).

[16] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[17] J.P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschrig (Akademie-Verlag, Berlin, 1991), p. 11.

[18] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[19] J. Furthmüller, P. Käckell, F. Bechstedt, and G. Kresse, Phys. Rev. B **61**, 4576 (2000).

[20] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996); Phys. Rev. B **54**, 11 169 (1996).

[21] H.J. Monkhorst and J.D. Pack, Phys. Rev. B **13**, 5188 (1976).

[22] A. Mainwood, J.E. Lowther, and J.A. van Wyk, J. Phys.: Condens. Matter **5**, 7929 (1993).