

Prediction of a low-spin ground state in the GaAs:V²⁺ impurity system

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All 3d impurities observed to date in tetrahedral semiconductors have a high-spin ground state, in agreement with Hund's rule. Using first-principles self-consistent Green's-function calculations for substitutional GaAs:V within the local-spin-density formalism, we predict that the as-yet unobserved ground state of GaAs:V²⁺ is of the low-spin type. The origin of this unusual ground state is explained.

INTRODUCTION AND STATEMENT OF PROBLEMS

The 3d orbitals of a transition-atom impurity in a cubic semiconductor can be split by the crystal field (CF) into t_2 and e orbitals, each being further split by the exchange (X) interaction into spin-up (t_+, e_+) and spin-down (t_-, e_-) components¹ (Fig. 1). Depending on the relative order of the orbital energies ϵ_e^+ , ϵ_e^- , ϵ_t^+ , and ϵ_t^- , the electronic ground state of the N impurity d electrons can correspond either to a maximum electronic spin S ("high spin" or "Hund's rule state") or to a lower spin ("low spin"). Electron-paramagnetic-resonance (EPR) measurements of S known to date for 3d impurities in Si, Ge, III-V, and II-VI semiconductors¹⁻⁵ (over 90 different systems comprising various charge states of the impurities Ti through Cu in different host crystals), have shown exclusively high-spin ground states. This universality has suggested¹ (see Fig. 1) that the one-electron exchange energies ($\Delta_x^t = \epsilon_e^+ - \epsilon_e^-$ and $\Delta_x^e = \epsilon_t^+ - \epsilon_t^-$) uniformly outweigh crystal-field energies ($\Delta_{CF} = \epsilon_t - \epsilon_e$). Electronic-structure calculations⁶⁻¹¹ on a number of representative systems have generally¹² concurred with this conclusion. Recent careful analysis of the absorption spectra of 3d impurities in III-V and II-VI semiconductors¹³ has suggested, however, that whereas in a given semiconductor Δ_{CF} increases as the impurity's atomic number Z decreases away from Mn (e.g., Mn → Cr

→ V → Ti), the exchange splitting Δ_x (or, in general, the many-electron correction) decreases in the same direction in the periodic table. This has raised the possibility^{9,13,14} that the generally negative spin-reference parameter $\delta = (\Delta_{CF} - \Delta_x)/\Delta_x$ might change sign at the low- Z limit of the 3d series, giving rise to an unprecedented low-spin ground state in a semiconductor. To quantitatively examine this possibility, we have carried out first-principles spin-unrestricted self-consistent Green's-function calculations for substitutional 3d impurities in GaAs. We find that the hitherto unobserved ground state of GaAs:V²⁺ is of a low-spin symmetry, in violation of Hund's rule. Results for other 3d impurities in GaAs will be discussed elsewhere; here we present our results for GaAs:V and discuss the electronic mechanism leading to its unusual ground state and the implications for theories of deep impurities in semiconductors.

For a fixed number $2 \leq N \leq 10$ of impurity d electrons, the ground-state configuration (n^*, m^*, p^*) in a spin-unrestricted formalism is the one which minimizes the total energy $E^{(N)}(e_+^n e_-^{2-n} t_+^m t_-^{3-m})$ (where $N = 10 - n - m - p$ and $n \leq 2$; $m, p \leq 3$, consistent with the degeneracies), giving thereby an observable net electron spin $S^{(N)} = 5 - m^* - N/2$. Occupying these levels in increasing order of their energies ($\Delta_x > 0$ and for substitutional tetrahedral symmetry¹ $\Delta_{CF} > 0$) gives for $3 \leq N \leq 6$ more than one possible solution (Fig. 1): a low-spin ground state if $\delta > 0$ (the e_- orbital is occupied in preference to t_+) or a high-spin ground state if $\delta < 0$ (the t_+ orbital is occupied in preference to e_-). Each solution is characterized by its spin S , as well as by its g value and hyperfine coupling constant, and hence could, in principle, be identified in an EPR experiment. Since, however, the data on GaAs:V (see below) are still fragmentary, it has not been possible to determine if the ground state for $N = 3$ (V²⁺) is low spin $e_+^2 e_-^1 t_+^0 t_-^0$ (²E, $S = \frac{1}{2}$), or high spin $e_+^2 e_-^1 t_+^0 t_-^0$ (⁴T₁, $S = \frac{3}{2}$).

ELECTRONIC STRUCTURE

We have calculated self-consistently the electronic structure of the V³⁺ ($N = 2$) and V²⁺ ($N = 3$) impurity at the ideal Ga substitutional tetrahedral site in GaAs within the self-interaction-corrected¹⁵ local-spin-density formalism. We have used our Green's-function method described previously,¹⁰ retaining all core and valence orbitals of the impurity as spin-polarizable states. We have modeled the host crystal in a local pseudopotential framework, adjusting the pseudopotential to reproduce the observed band structure of pure GaAs. The spin-polarized local density of states (LDOS) of

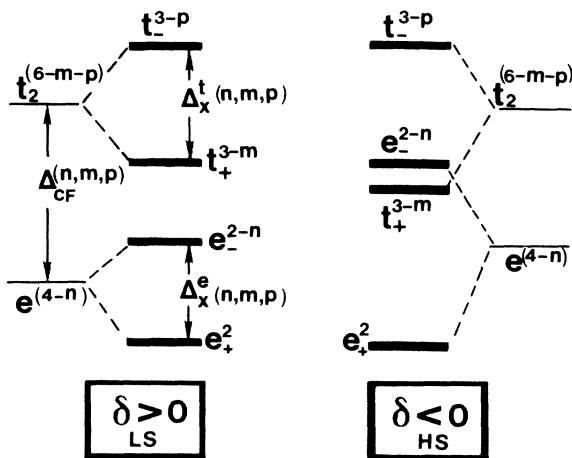


FIG. 1. Schematic energy-level diagram for a d orbital in substitutional tetrahedral symmetry, showing the low-spin (LS) [$\delta = (\Delta_{CF} - \Delta_x)/\Delta_x > 0$] and high-spin (HS) ($\delta < 0$) cases.

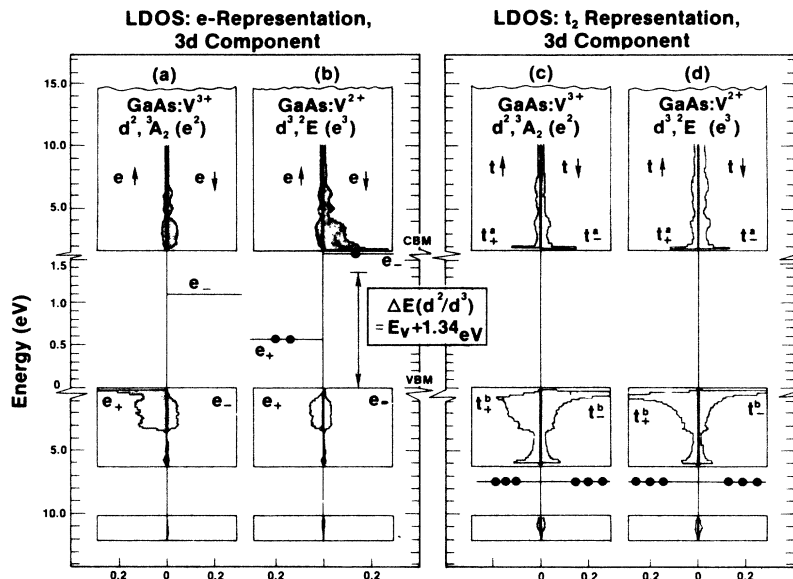


FIG. 2. Calculated local density of states (3d component only) of the V-induced e and t_2 levels in GaAs showing spin-up (+) and spin-down (-), bonding (b) and antibonding (a) levels. Occupation of gap levels is denoted by solid circles, shaded areas denote valence-band resonances, a_1 levels not shown (see text).

the impurity-induced e and t_2 levels are shown in Fig. 2, choosing the valence-band maximum (E_v) as energy reference. We find that V introduces a fully occupied t_2 bound state in the GaAs heteropolar gap at $E_v - 7.3$ eV (as well as an a_1 bound state 1 eV below it). In the energy range between E_v and $E_v - 6.5$ eV (the upper valence band of GaAs) we find three types of impurity-induced levels: the t_2 and e “crystal-field resonances”^{5,9} (bonding and non-bonding V-As combinations, respectively) and the a_1 resonances (at $E_v - 1$ eV, not shown in Fig. 2). The antibonding (a) counterparts of these levels appear as empty states in the conduction band, and include the t_2^a and e^a “dangling bond hybrids”^{5,9} (V p and d orbitals, strongly hybridized with Ga and As p orbitals) and a_1 resonances (at $E_v + 5.2$ eV, not shown). Whereas the conduction-band resonances have small exchange splittings, we find in the band-gap region the strongly exchange split localized e levels. The energy-level scheme obtained here is similar to that inferred in spin-restricted calculations for 3d impurities in GaP.⁹

(L) magnetic moment in the impurity subspace $\mu_L = 1.30\mu_B$, far reduced relative to the total magnetic moment over the entire space, $\mu = 2S = 2\mu_B$. μ_L is contributed exclusively by the impurity-induced valence-band resonances (i.e., $\mu_{\text{gap}} = 0$) of e type ($+1.42\mu_B$) and t_2 type ($-0.12\mu_B$). We find a negative spin density at the impurity nucleus (a consequence of core polarization) and that most (65%) of the spin density is localized on the impurity, the remaining 35% being delocalized outside the impurity

GaAs:V³⁺

For the $N=2$ case of GaAs:V³⁺ there is no distinction between low- and high-spin states. We find the ground-state configuration to be $e_+^2 e_0^0 t_+^0 t_0^0$ (3A_2) with an empty e_- level in the gap at $E_v + 1.095$ eV. The calculated ground-state properties of this system are summarized in Fig. 3(a): The calculated¹⁰ spin ($S=1$), g value (1.9582), and ⁵¹V hyperfine coupling constant ($A = -38.4 \times 10^{-4} \text{ cm}^{-1}$) are consistent with experiment¹⁴ ($S=1$, $g=1.957$, and $A = \pm 54 \times 10^{-4} \text{ cm}^{-1}$, or¹⁶ $55 \times 10^{-4} \text{ cm}^{-1}$). The reduction of A from its value in ionic systems (e.g.,⁵ $76.1 \times 10^{-4} \text{ cm}^{-1}$ for CaO:V²⁺) and that of g from its spin-only value (2.0023) both indicate substantial covalency (since the g shift has a contribution^{1,10} from the momentum matrix element of p and d orbitals, and hence increases with covalency). Consistent with this covalency, we find that the local

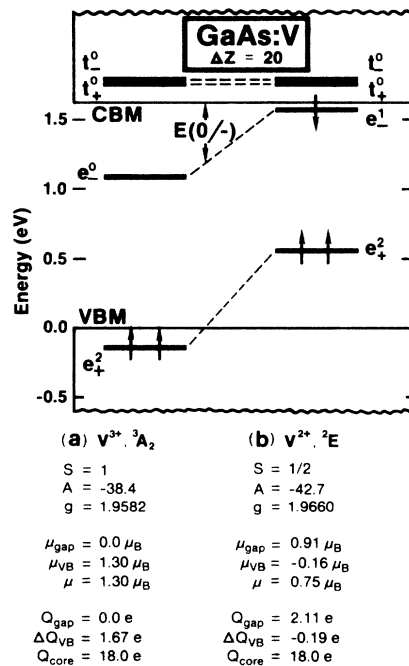


FIG. 3. Calculated ground-state properties of the V³⁺ [in (a)] and V²⁺ [in (b)] impurity in GaAs. The hyperfine coupling constant A is in units of 10^{-4} cm^{-1} .

subspace. This is consistent with a qualitative analysis¹⁶ of the electron-nuclear-double-resonance (ENDOR) data,¹⁶ which suggest that most $(79.7 - X)\%$ of the spin density is on the V^{3+} site, 20.3% is on the first two shells of neighbors, and an undetermined (but smaller¹⁶) amount $X\%$ is delocalized on further shells of ligands. The spin-allowed excited electronic states of V^{3+} should correspond in our model to the $e_{\uparrow}^2 t_{\uparrow}^0 (^3A_2) \rightarrow e_{\uparrow}^1 t_{\uparrow}^1 (^3T_2)$ and $e_{\uparrow}^2 t_{\uparrow}^0 (^3A_2) \rightarrow e_{\uparrow}^0 t_{\uparrow}^2 (^3T_1)$ transitions, observed for V^{3+} in a number of III-V semiconductors.^{2,17}

GaAs: V^{2+}

For the $N=3$ case of GaAs: V^{2+} , an additional electron needs to be accommodated either in the e_{-} or in the t_{+} orbitals. We find that the ground state corresponds to the former, low-spin situation, i.e., to $e_{\uparrow}^2 e_{\downarrow}^1 t_{\uparrow}^0 t_{\downarrow}^0, ^2E$. To check the stability of this calculated ground state relative to a possible high-spin ground state, we have calculated the energy difference $\Delta E = E^{(3)}(e_{\uparrow}^2 e_{\downarrow}^0 t_{\uparrow}^1, ^4T_1) - E^{(3)}(e_{\uparrow}^2 e_{\downarrow}^1 t_{\uparrow}^0, ^2E)$ by imposing on the self-consistent calculation an initial guess for the impurity potential which artificially favors the high-spin state (i.e., a large Δ_{ξ} or $\delta < 0$ in Fig. 1). This total energy difference can be approximated in the transition-state construct as the difference in orbital energies $\epsilon_{\uparrow}^+ - \epsilon_{\downarrow}^-$, calculated at the intermediate occupation $e_{\uparrow}^2 e_{\downarrow}^0 t_{\uparrow}^0 t_{\downarrow}^0$. In all cases we find that at the self-consistency limit a low-spin $\delta > 0$ solution is obtained, hence $\Delta E > 0$. The following approximations in our calculation may affect this conclusion: (i) neglect of static and dynamic Jahn-Teller (JT) coupling (expected to be small in the 2E state of V^{2+} , in analogy with the ~ 0.02 eV JT energy¹⁸ of the 2E states of Ni^{+} in II-VI semiconductors), (ii) neglect of symmetric (outward) relaxations¹⁹ (expected to be stronger in the high-spin 4T_1 state than in the low-spin 2E state, stabilizing the former), (iii) neglect of dynamic orbital (i.e., configuration mixing) correlation effects (calculated in Ref. 13 to be only around -0.1 eV both for 4T_1 and for 2E), and (iv) the possibility that the strong t_{\uparrow}^2 resonance of V^{2+} near the conduction-band minimum [Fig. 2(d)] will be stabilized by effective-mass effects, leading to a shallow high-spin bound state (inconsistent with the rather deep observed acceptor level²⁰).

No EPR or ENDOR data exist for GaAs: V^{2+} ; our predictions are given in Fig. 3(b). Interestingly, we find that, in contrast to V^{3+} , most of the local magnetic moment in V^{2+} ($\mu_L = 0.75\mu_B$, $\mu = 1.0\mu_B$) is contributed by the band-gap levels ($\mu_{\text{gap}} = 0.91\mu_B$), with only a small (negative) portion ($\mu_{\text{VB}} = -0.16\mu_B$) contributed by the valence-band resonances. The low-energy electronic excitations of V^{2+} correspond in our picture to the spin-forbidden $e_{\uparrow}^2 e_{\downarrow}^1 (^2E) \rightarrow e_{\uparrow}^2 t_{\uparrow}^1 (^4T_1)$ and spin-allowed $e_{\uparrow}^2 e_{\downarrow}^1 (^2E) \rightarrow e_{\uparrow}^2 t_{\uparrow}^1 (^2T)$ transitions. The optical spectra will be discussed elsewhere.¹⁷

Having obtained the predicted ground states of V^{2+} and V^{3+} , we are in a position to calculate the ionization energy $V^{2+} \rightarrow V^{3+} + e$, i.e., the acceptor level. Using the transition-state construct, this difference $\Delta E(d^2/d^3)$ in total energies $E^{(3)}(e_{\uparrow}^2 e_{\downarrow}^1) - E^{(2)}(e_{\uparrow}^2 e_{\downarrow}^0)$ is approximated as the position of the e_{-} orbital calculated self-consistently at the intermediate $e_{\uparrow}^2 e_{\downarrow}^0$ configuration. This gives an acceptor energy $\Delta E(d^2/d^3) = E_v + 1.34$ eV (Fig. 2), close to the observed value²⁰ $E_v + 1.38$ eV. The donor transition energy $\Delta E(d^1/d^2) = E^{(2)}(e_{\uparrow}^2) - E^{(1)}(e_{\uparrow}^1)$ is located in our calcula-

tion inside the valence band (where the e_{+} resonance is; see Fig. 2), consistent with the fact that the internal excitations of V^{3+} are observed even if the Fermi energy is inside the valence band.²⁰ Our results hence suggest that isolated substitutional V in GaAs cannot explain a midgap electrical level needed to rationalize its semi-insulating behavior;¹⁴ a complex involving V may be a more likely candidate.

DISCUSSION

In an interacting electron system which sustains localized states, the effective one-particle energies depend on the occupation numbers of all levels in the system. Figure 2 shows indeed that occupation of the empty e_{-} level of V^{3+} by an electron (creating thereby V^{2+}) raises its energy by (the effective Mott-Hubbard energy) $U(\underline{ee}) = 0.495$ eV and that of e_{+} by $U(\underline{ee}) = 0.696$ eV (due to increased electron repulsion between e_{+} and e_{-}). The reason these effective Coulomb energies are so much smaller than the free ion value for V [17.4 eV (Ref. 21)] is that, in a semiconductor, charge redistributes itself in response to impurity ionization to minimize its effect (a "self-regulating response"²²). This can be illustrated as follows: The two e_{\uparrow}^2 electrons of V^{3+} contribute an effective charge of $1.67e$ to the impurity subspace [ΔQ_{VB} in Fig. 3(a)], whereas the three $e_{\uparrow}^2 e_{\downarrow}^1$ electrons of V^{2+} contribute an effective gap charge of $Q_{\text{gap}} = 2.11e$, but the valence-band resonances diminish their amplitude on the impurity site ($\Delta Q_{\text{VB}} = -0.19e$), leading to a total valence charge of $Q_{\text{gap}} + \Delta Q_{\text{VB}} = 1.92e$, i.e., only 0.25e more than in V^{3+} . The strong hybridization evidenced by this behavior as well as by the reduction of μ_L relative to μ (i.e., $\mu_L/\mu = 0.75$) also holds the key to understanding the low-spin state of V^{2+} . Since e orbitals in substitutional tetrahedral symmetry have lobes pointing to the *next*-nearest neighbors,¹ they remain only weakly hybridized with their first neighbors throughout the $3d$ series (forming weak π bonds). Their localization is manifested by substantial exchange splittings, e.g., $\Delta_{\xi} = 1.03$ and 1.23 eV for V^{2+} and V^{3+} , respectively. In contrast, since the lobes of the t_2 orbitals point to the *first*-nearest neighbors, they are capable of forming stronger σ bonds whose degree of hybridization depends on the availability of host t_2 LDOS at the energy of the respective impurity-atom d level. At the center of the $3d$ series the atomic $3d_t$ orbitals are too deep to experience a high host t_2 LDOS, but at the low- Z limit of the series, the shallower atomic $3d_t$ orbitals have available to them a high LDOS of host t_2 orbitals near the band edges. This leads to effectively hybridized and delocalized t_{\uparrow}^2 levels in GaAs:V, having hence vanishingly small exchange splitting $\Delta_{\xi} \approx 0$ (see Fig. 2). This large disparity in the degree of hybridization of e and t_2 levels ("differential hybridization"¹³) at the low- Z end of the $3d$ series leads to a large crystal-field splitting Δ_{CF} (e.g., relative to Mn), which for V exceeds Δ_X , giving rise to a low-spin ground state. In contrast, in more ionic host crystals (e.g., II-VI's), the t_{\uparrow}^2 orbitals are inside the (wider) band gap; hence they are more localized. This leads to a smaller Δ_{CF} and larger Δ_X , i.e., to a high-spin ground state. This delicate, occupation-dependent balance between $\Delta_X(n,m,p)$ and $\Delta_{\text{CF}}(n,m,p)$ together with band-structure effects (correct energy dependence of the LDOS) need to be incorporated in impurity models to correctly describe ground-state spin multiplicities. This discussion suggests that as we move from $3d$

to 4d and 5d impurities (e.g., $V \rightarrow Nb \rightarrow Ta$, or $Cr \rightarrow Mo \rightarrow W$) the increased covalency will further reduce Δ_X (and, in general, the many-electron effects), leading to a prevalence of low-spin ground states.

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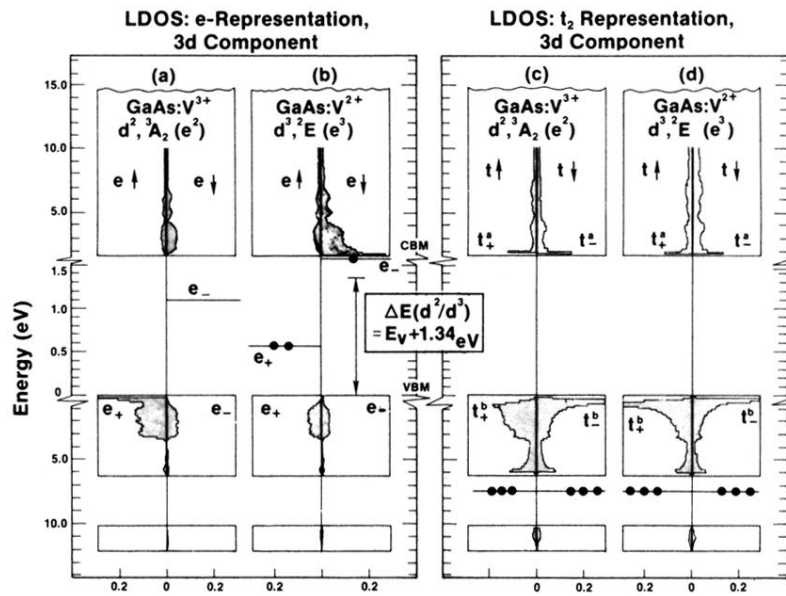


FIG. 2. Calculated local density of states ($3d$ component only) of the V-induced e and t_2 levels in GaAs showing spin-up (+) and spin-down (-), bonding (b) and antibonding (a) levels. Occupation of gap levels is denoted by solid circles, shaded areas denote valence-band resonances, a_1 levels not shown (see text).