Prediction of a low-spin ground state in the GaAs:V$^{2+}$ impurity system

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All 3$d$ 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:V$^{2+}$ is of the low-spin type. The origin of this unusual ground state is explained.

INTRODUCTION AND STATEMENT OF PROBLEMS

The 3$d$ orbitals of a transition-atom impurity in a cubic semiconductor can be split by the crystal field (CF) into $t_{2g}$ and $e$ orbitals, each being further split by the exchange $(X)$ interaction into spin-up $(t_{+,e+})$ and spin-down $(t_{-,e-})$ components (Fig. 1). Depending on the relative order of the orbital energies $e_{t^+}^n$, $e_{t^+}^o$, $e_{t^+}^s$, and $e_{t^+}^p$, 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 3$d$ impurities in Si, Ge, III-V, and II-VI semiconductors (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 suggested (see Fig. 1) that the one-electron exchange energies $\Delta_{CF} = e_{t^+}^n - e_{t^+}^o$ and $\Delta_{CF}^\neq = e_{t^+}^o - e_{t^+}^p$ uniformly outweigh crystal-field energies $\Delta_{CF} = e_{t^+}^n - e_{t^+}^o$. Electronic-structure calculations (see Fig. 1) on a number of representative systems have generally concurred with this conclusion. Recent careful analysis of the absorption spectra of 3$d$ impurities in III-V and II-VI semiconductors has suggested, however, that whereas in a given semiconductor $\Delta_{CF}$ increases as the impurity’s atomic number $Z$ decreases away from Mn (e.g., Mn$\rightarrow$Cr$\rightarrow$V$\rightarrow$Ti), the exchange splitting $\Delta_X$ (or, in general, the many-electron correction) decreases in the same direction in the periodic table. This has raised the possibility that the generally negative spin-reference parameter $\delta = (\Delta_{CF} - \Delta_X)/\Delta_X$ might change sign at the low-$Z$ limit of the 3$d$ 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 3$d$ impurities in GaAs. We find that the hitherto unobserved ground state of GaAs:V$^{2+}$ is of a low-spin symmetry, in violation of Hund’s rule. Results for other 3$d$ 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 $(n^s,m^p,p^p)$ in a spin-unrestricted formalism is the one which minimizes the total energy $E^{(N)}(e_{t^+}^n, e_{t^+}^o, e_{t^+}^s, e_{t^+}^p)$ (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 $S^{(N)} = S - m^s - N/2$. Occupying these levels in increasing order of their energies ($\Delta_X > 0$ and for substitutional tetrahedral symmetry $\Delta_{CF} > 0$) 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 $N = 3$ ($V^{2+}$) is low spin $e_{t^+}^n, e_{t^+}^o, t_{+}^p, t_{+}^s$ (4$T_1$, $S = \frac{1}{2}$), or high spin $e_{t^+}^n, e_{t^+}^o, t_{+}^p, t_{+}^s$ (4$T_1$, $S = \frac{1}{2}$).

ELECTRONIC STRUCTURE

We have calculated self-consistently the electronic structure of the $V^{3+}$ $(N = 2)$ and $V^{2+}$ $(N = 3)$ impurity at the ideal Ga substitutional tetrahedral site in GaAs within the self-interaction-corrected local-spin-density formalism. We have used our Green’s-function method described previously, 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...
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 $E_v - 7.3\,\text{eV}$ (as well as an $a_1$ bound state 1 eV below it). In the energy range between $E_v$ and $E_v - 6.5\,\text{eV}$ (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 $E_v - 1\,\text{eV}$, not shown in Fig. 2). The antibonding ($a$) counterparts of these levels appear as empty states in the conduction band, and include the $t'^2$ and $e'^2$ "dangling bond hydrids" $^5,9$ ($V\,p$ and $d$ orbitals, strongly hybridized with Ga and As $p$ orbitals) and $a_1$ resonances (at $E_v + 5.2\,\text{eV}$, 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 3$d$ impurities in GaP. $^9$

\begin{center}
\textbf{GaAs:V$^{2+}$}
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For the $N = 2$ case of GaAs:V$^{2+}$ there is no distinction between low- and high-spin states. We find the ground-state configuration to be $e\,^2_d\,^2_e\,^2_d'\,^2_e'$ (\(t^2_A\)) with an empty $e$-level in the gap at $E_v + 1.095\,\text{eV}$. The calculated ground-state properties of this system are summarized in Fig. 3(a): The calculated $^4$ spin ($S = 1$), $g$ value (1.9582), and $^{35}$V hyperfine coupling constant ($A = -38.4\times 10^{-4}\,\text{cm}^{-1}$) are consistent with experiment $^4$ ($S = 1$, $g = 1.957$, and $A = \pm 54\times 10^{-4}\,\text{cm}^{-1}$, or $^{16}55\times 10^{-4}\,\text{cm}^{-1}$). The reduction of $A$ from its value in ionic systems (e.g., $76.1\times 10^{-4}\,\text{cm}^{-1}$ for CaO:V$^{2+}$) and that of $g$ from its spin-only value (2.0023) both indicate substantial covalency (since the $g$ shift has a contribution $^9$ from the momentum matrix element of $p$ and $d$ orbitals, and hence increases with covalency). Consistent with this covalency, we find that the local ($L$) magnetic moment in the impurity subspace is $\mu_L = 1.30\mu_B$, far reduced relative to the total magnetic moment over the entire space, $\mu = 2S = 2\mu_B$. $\mu_L$ is contributed exclusively by the impurity-induced valence-band resonances (i.e., $\mu_{\text{imp}} = 0$) 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 located on the impurity, the remaining 35% being delocalized outside the impurity.

\begin{center}
\textbf{FIG. 2.} Calculated local density of states (3$d$ component only) of the V-induced $e$ and $t_2$ levels is 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).
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\textbf{FIG. 3.} Calculated ground-state properties of the V$^{3+}$ [in (a)] and V$^{2+}$ [in (b)] impurity in GaAs. The hyperfine coupling constant $A$ is in units of $10^{-4}\,\text{cm}^{-1}$.
\end{center}
subspace. This is consistent with a qualitative analysis\textsuperscript{16} of the electron-nuclear double-resonance (ENDOR) data,\textsuperscript{16} which suggest that most (79.7% - \(\chi\)% of the spin density is on the \(V^{3+}\) site, 20.3% is on the first two shells of neighbors, and an undetermined (but smaller\textsuperscript{19}) amount \(\chi\)% is delocalized on further shells of ligands. The spin-allowed excited electronic states of \(V^{3+}\) should correspond in our model to the \(e_1\ell_2^\pi (\tilde{A}_1) \rightarrow e_1\ell_2^\pi (\tilde{T}_2)\) and \(e_1\ell_2^\pi (\tilde{A}_1) \rightarrow e_2\ell_2^\pi (\tilde{T}_2)\) transitions, observed for \(V^{3+}\) in a number of III-V semiconductors.\textsuperscript{2,17}

\textbf{GaAs:V\textsuperscript{2+}}

For the \(N = 3\) case of GaAs:V\textsuperscript{2+}, an additional electron needs to be accommodated either in the \(e_-\) or in the \(\ell_\pi\) orbitals. We find that the ground state corresponds to the former, low-spin situation, i.e., to \(e_1\ell_2 \ell_2^\pi (\tilde{E})\). To check the stability of this calculated ground state relative to a possible high-spin ground state, we have calculated the energy difference \(\Delta E = E(\tilde{E}) - E(\tilde{4}\tilde{T}_1)\) 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 \(\Delta\) or \(\delta < 0\) in Fig. 1). This total energy difference can be approximated in the transition-state construct as the difference in orbital energies \(\epsilon_2^+ - \epsilon_2^-\), calculated at the intermediate occupation \(e_2^+ e_2^\pi^\downarrow e_2^\pi^\uparrow\). 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 \(\tilde{E}\) state of \(V^{2+}\), in analogy with the \(\approx 0.02\) eV JT energy\textsuperscript{18} of the \(\tilde{E}\) states of Ni\textsuperscript{2+} in III-V semiconductors), (ii) neglect of symmetric (outward) relaxations\textsuperscript{19} (expected to be stronger in the high-spin \(4\tilde{T}_1\) state than in the low-spin \(\tilde{2}\tilde{E}\) 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 \(4\tilde{T}_1\) and for \(\tilde{2}\tilde{E}\)), and (iv) the possibility that the strong \(\ell_2^\pi\) 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 occupied acceptor level\textsuperscript{20}).

No EPR or ENDOR data exist for GaAs:V\textsuperscript{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 (\(\mu_{\pi} = -0.91 \mu_B\)), with only a small (negative) portion (\(\mu_{\nu} = -0.16 \mu_B\)) contributed by the valence-band resonances. The low-energy electronic excitations of \(V^{2+}\) correspond in our picture to the spin-forbidden \(e_2^+ e_2^\pi^\downarrow (\tilde{2}\tilde{E}) \rightarrow e_2^+ \ell_2^\pi^\downarrow (\tilde{4}\tilde{T}_1)\) and spin-allowed \(e_2^+ e_2^\pi^\downarrow (\tilde{2}\tilde{E}) \rightarrow e_2^\pi^\downarrow (\tilde{4}\tilde{T}_2)\) transitions. The optical spectra will be discussed elsewhere.\textsuperscript{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 \(\Delta E(\ell_2 / \ell_2^\pi)\) in total energies \(E(\ell_2) - E(\ell_2^\pi)\) is approximated as the position of the \(e_-\) orbital calculated self-consistently at the intermediate \(e_2^+ e_2^\pi^\downarrow\) configuration. This gives an acceptor energy \(\Delta E(\ell_2 / \ell_2^\pi) = E_+ + 1.34\) eV (Fig. 2), close to the observed value\textsuperscript{20} \(E_+ = 1.38\) eV. The donor transition energy \(\Delta E(\ell_2^\pi / \ell_2) = E(\ell_2) - E(\ell_2^\pi)\) is located in our calculation 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.\textsuperscript{20} Our results hence suggest that isolated substitutional V in GaAs cannot explain a midgap electrical level needed to rationalize its semi-insulating behavior;\textsuperscript{14} a complex involving V may be a more likely candidate.

\section*{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) \(U(e^0) = 0.495\) eV and that of \(e_+\) by \(U(e^0) = 0.696\) 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"\textsuperscript{22}). This can be illustrated as follows: the two \(e_+^\dagger\) electrons of \(V^{3+}\) contribute an effective charge of 1.0 e to the impurity subspace \(\Delta Q_{VB}\) in Fig. 3(a), whereas the three \(e_-^\dagger\) electrons of \(V^{2+}\) contribute an effective gap charge of \(\Delta Q_{gap} = 2.11\) e, but the valence-band resonances diminish their amplitude on the impurity site (\(\Delta Q_{VB} = -0.19\) e), leading to a total valence charge of \(Q_{VB} + \Delta Q_{VB} = 1.92\) e, i.e., only 0.25 e more than in \(V^{3+}\). The strong hybridization evidenced by this behavior as well as by the reduction of \(\mu_\ell/\mu\) relative to \(\mu\) (i.e., \(\mu_\ell/\mu = 0.75\)) also holds the key to understanding the low-spin state of \(V^{2+}\). Since \(e^\pm\) orbitals in substitutional tetrahedral symmetry have lobes pointing to the nearest neighbors,\textsuperscript{1} they remain only weakly hybridized with their first neighbors throughout the 3d series (forming weak \(\pi\) bonds). Their localization is manifested by substantial exchange splittings, e.g., \(\Delta e = 1.03\) 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 \(\sigma\) 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 \(3d\) orbitals are too deep to experience a high host \(t_2\) LDOS, but at the low-\(Z\) limit of the series, the shallower atomic \(3d\) orbitals have available to them a high LDOS of host \(t_2\) orbitals near the band edges. This leads to effectively hybridized and delocalized \(t_2\) levels in GaAs:V, hence vanishingly small exchange splitting \(\Delta e = 0\) (see Fig. 2). This large disparity in the degree of hybridization of \(e_+\) and \(t_2\) levels ("differential hybridization"\textsuperscript{12}) at the low-\(Z\) end of the 3d series leads to a large crystal-field splitting \(\Delta_{CF}\) (i.e., relative to Mn), which for V exceeds \(\Delta e\), giving rise to a low-spin ground state. In contrast, in more ionic host crystals (i.e., II-VI's), the \(t_2\) orbitals are inside the (wider) band gap; hence they are more localized. This leads to a smaller \(\Delta_{CF}\) and larger \(\Delta e\), i.e., to a high-spin ground state. This delicate, occupation-dependent balance between \(\Delta e(n,m,p)\) and \(\Delta_{CF}(n,m,p)\) 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 → Nb → Ta, or Cr → Mo → W) the increased covalency will further reduce $\Delta_{\chi}$ (and, in general, the many-electron effects), leading to a prevalence of low-spin ground states.

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2References 10 and 11 predicted as-yet unobserved low-spin ground states for interstitial Ti, Ti, V, and V+ impurities in Si.


12References 10 and 11 predicted as-yet unobserved low-spin ground states for interstitial Ti, Ti, V, and V+ impurities in Si.


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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).