

# Theoretical investigation of the electrical and optical activity of vanadium in GaAs

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(Received 31 December 1985)

We study the excitation and ionization processes at the isolated substitutional vanadium impurity in GaAs. The electronic structure is solved through the spin-restricted version of the multiple-scattering  $X\alpha$  method to obtain the relevant mean-field energies, and correlation effects are evaluated through the Fazzio-Caldas-Zunger multiplet approach. The similar systems GaP:V, InP:V are also investigated. Our results for GaAs:V point to the occurrence of an acceptor level at  $\sim E_c - 0.16$  eV, the donor level appearing very close to or within the valence band. The V-related midgap acceptor should then be related to some complex defect involving vanadium. We also suggest that  $V^{2+}$  in these compounds is present in the low-spin ground state  ${}^2E$ .

## I. INTRODUCTION

Transition metals, particularly those from the  $3d$  series, have probably been the most intensively studied group of deep-level impurities in covalent semiconductors<sup>1-5</sup> in the past few years. Much insight was gained into the properties of these rather complex systems, both from experimental<sup>1-3</sup> and theoretical<sup>4,5</sup> studies (these latter with the application of new nonempirical models<sup>4-9</sup>).

A number of features are now apparent for  $3d$  impurity centers in III-V compounds (GaAs, GaP, InP). The  $3d$  metals ( $T$ ) from Cr to Ni introduce at least one deep acceptor level in the band gap of the semiconductor.<sup>1-3</sup> The metal enters at a regular lattice site substituting for the cation,<sup>3</sup> hence the neutral charge state ( $A^0$ ) of the defect corresponds to the oxidation state  $T^{3+}$ ; the first acceptor level  $E_A(-/0)$  corresponds to the transition  $T^{3+} \rightarrow T^{2+}$ .<sup>3-5</sup> Optical activity (internal or intra- $d$  absorption or luminescence) has been detected<sup>3,5</sup> for the  $T^{2+}$  impurities indicating that many-electron multiplet effects within the open  $d$  shell were a relevant feature of the systems.<sup>5</sup> On the other hand, the occurrence of the first acceptor level for all of these impurities, coupled to the appearance of up to four charge states for the same impurity [Cr in GaAs (Ref. 3)] points to the basic relevance of covalency or hybridization effects<sup>5</sup> [reducing  $U$ , the Mott-Hubbard energy<sup>10</sup> for the impurity center]. Vibronic coupling to the lattice, as well as lattice relaxation effects were also shown to play a role in the description of the optical and electrical properties of the systems.<sup>3-5</sup>

One of the most exciting results that emerged from this systematic investigation of  $3d$  impurities was that state-of-the-art theoretical methods, within the mean-field approximation,<sup>6-9</sup> can yield realistic descriptions of the defect centers once multiplet effects are taken properly into account.<sup>5</sup>

We propose here to investigate the vanadium impurity center in GaAs, for which a wealth of experimental data is already available,<sup>2(b),3,11-19</sup> and which is not fully un-

derstood at present.<sup>3</sup> Mean-field calculations are done within the multiple-scattering (MS)  $X\alpha$  cluster model with the Watson-sphere boundary condition,<sup>7</sup> and the Fazzio, Caldas, and Zunger<sup>5</sup> (FCZ) method is used for inclusion of multiplet effects. We discuss in the next section the experimental evidence<sup>2(b),3,11-19</sup> concerning the properties of GaAs:V, and also the closely related systems GaP:V and InP:V.<sup>3,14,16,19-26</sup> It is seen that information from one center can help us understand the others, as much of the mean-field effects are common to the III-V class of compounds.<sup>3,4,27,28</sup> Our mean-field results for GaAs:V are presented in Sec. III, together with a discussion on multiplet effects. It is shown that vanadium presents unique characteristics, and that the evidence is compatible with an earlier suggestion<sup>5</sup> that  $V^{2+}$  would be present in covalent III-V compounds in a low-spin state.

## II. III-V:V—EXPERIMENTAL SITUATION

An excellent survey of the experimental data for vanadium in GaAs, GaP, and InP is given in Ref. 3. Optical activity from V center in GaAs (Refs. 3, 11-16, and 18) comprises a distinctive photoluminescence (PL) spectrum, which counterpart, together with the excitation spectrum (PLE), is also seen in absorption.

The strong V-related luminescence band is also seen in GaP (Ref. 14) and InP,<sup>20-22</sup> and is very similar for the three compounds. As shown schematically in Fig. 1, it consists of a strong zero phonon line (ZPL) with an accompanying hot line (HZPL), followed by phonon replicas (P); the whole structure is further replicated<sup>21</sup> by a local-mode phonon (LM) to lower energies. The strength of the phonon coupling is slightly material dependent.<sup>14,21</sup> Apart from the specific energies for the lines (indicated in the figure) the overall structure is strikingly similar. The doublet splitting of the ZPL's (both cold and hot) shown in the insert of Fig. 1 is seen clearly<sup>14</sup> in GaP ( $\sim 0.1$  meV), is barely discernible<sup>14</sup> in GaAs and apparently disappears<sup>17</sup> in InP.

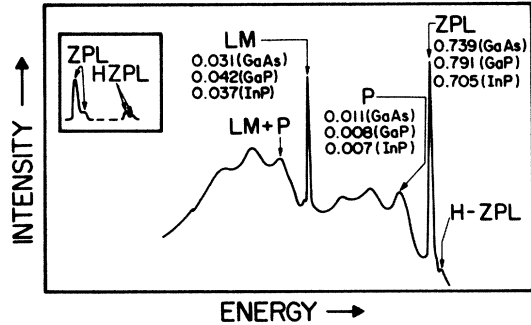


FIG. 1. Schematic representation of the luminescent transition of V centers in GaAs, GaP, and InP (not in scale). Energies for the lines, in eV, are indicated for the three compounds. Insert shows scheme of the doublet splitting of the no-phonon lines.

Zeeman spectroscopy of the main ZPL (Refs. 14 and 21) shows that it splits in six lines with a  $g$  factor close to the free-electron value; an important confirmation of the phonon coupling is that the same behavior is exhibited not only by the hot line, but also by the local-mode replica<sup>21</sup> in InP.

The absorption counterpart of the luminescence is seen in high-resistivity and in moderately  $n$ -type GaAs and InP,<sup>3</sup> and confirms the doublet character for the ZPL's.<sup>16</sup> The (weak) absorption band peaks at 0.79 eV in GaAs.<sup>19</sup>

The PLE band<sup>14-16,21</sup> is also seen in absorption, and presents a strongly temperature-dependent lineshape with two peaks (around 1.1 eV) converting to three at higher temperatures.<sup>11,13,15,23</sup> Also the absorption ZPL corresponding to the 1-eV band is seen for GaAs and InP,<sup>3</sup> with two other weak lines.<sup>16</sup>

Early analyses of the luminescence and PLE for GaAs and GaP ascribed the spectra to intra- $d$  transitions within the  $d^3$  shell of  $V^{2+}$  ( $A^-$ , acceptor state) (Refs. 12, 14, and 23). Mircea-Roussel *et al.*,<sup>13</sup> however, interpreted the temperature dependence of the 1-eV-absorption-band line shape as originating from a transition from an  $l=0$  ground state to an excited state with  $l=1$ , which would be compatible with the  ${}^3A_2({}^3F) \rightarrow {}^3T_1({}^3F)$  transition of  $V^{3+}$  ( $d^2$ , neutral state). It is to be noted that higher-Z  $3d$  impurities all present optical activity in the  $A^-$ ,  $T^{2+}$  state. Subsequent analyses of the V-related luminescence in InP by Skolnick *et al.*<sup>21</sup> presented strong evidence in favor of the  $V^{3+}$  interpretation: the study of the Zeeman splitting of the ZPL at high fields (up to 9.2 T) revealed that it is composed of three doublets, and that the doublet splitting occurs in the initial state of the transition. Furthermore, the  $g$  factors extracted from the data have values close to 2 for both ground and excited states. The analysis of the behavior under uniaxial stress<sup>22</sup> of the no-phonon lines of both luminescence and the 1-eV absorption (corresponding to the PLE band) in InP:V also points conclusively to the  $V^{3+}$  interpretation of the luminescence band.

As stated above, the strong similarity of the optical spectra for si-GaAs:V, GaP:V, and InP:V (where si denotes semi-insulating) indicates that a single interpretation should be valid for the three systems<sup>3,21,22</sup>.

Following Skolnick *et al.*,<sup>21</sup> the vanadium impurity is supposed to be in the  $3+$  oxidation state (neutral with respect to the lattice  $A^0$ ), with the high-spin ground state  ${}^3A_2({}^3F, e^2)$  of the  $d^2$  shell. The luminescent transition would correspond to  ${}^3T_2({}^3F, e^1 t^1) \rightarrow {}^3A_2({}^3F, e^2)$  with the excited state coupled to  $\epsilon$  (tetragonal) modes, which lowers the symmetry from  $T_2$  of  $T_d$  to  $B_2$  of  $D_{2d}$ . The no-phonon line splitting (1.5 meV) shown in the insert of Fig. 1 is accounted for by second-order spin-orbit coupling within the  ${}^3B_2$  state, and further splitting ( $<0.1$  meV) is caused by coupling of the different distortions (tunneling) via the spin-orbit interaction.<sup>22</sup> The excitation of luminescence would correspond to the transition  ${}^3A_2({}^3F, e^2) \rightarrow {}^3T_1({}^3F, e^1 t^1)$ , and in this case the excited state is coupled to  $\tau$  (trigonal) modes of distortion.<sup>3,13</sup>

Recent analyses of the temperature dependence of the absorption lineshape<sup>18</sup> in GaAs assuming strong dynamic coupling of the  ${}^3T_1$  state to  $\tau$  modes yield rather large Jahn-Teller energies of  $E_{JT} \approx 0.1$ . For si-GaAs and InP, two other lines are observed in absorption at 0.909 and 1.335 eV, and at 1.005 and 1.292 eV, respectively, which have also been ascribed to  $V^{3+}$ . Only for the larger-gap compound GaP the higher-lying spin-allowed transition  ${}^3A_2({}^3F, e^2) \rightarrow {}^3T_1({}^3P, t^2)$  has probably been observed in absorption at low temperatures ( $<180$  K), with a band around 1.756 eV (Refs. 16 and 23) [the original<sup>23</sup> assignment for this line was based on the  $V^{2+}$  interpretation]. A summary of the optical data for the systems is presented in Table I, where we enter also the absorption data for  $n$ -type GaAs:V, which has been ascribed to the acceptor ( $A^-$ ) state  $V^{2+}$ .<sup>3,16</sup>

For the si-GaAs samples where the V-related luminescence is observed, Kaufmann *et al.*<sup>14</sup> detect an isotropic EPR signal (already in the dark, from 20 to 80 K) with  $g$  factor 1.957, which is interpreted as arising from isolated cation-substitutional  $V^{3+}$  in agreement with the recent assignment of the PL transition. Recently Hage *et al.*<sup>25</sup> observed also the electron-nuclear double resonance (ENDOR) spectrum of GaAs:V<sup>3+</sup>, which can give a more detailed picture of the electronic spin density. The authors find a very strong localization of the wave function, with  $\sim 70\%$  over the impurity atom. In si-GaP:V samples<sup>24</sup> an EPR signal is also present, with was assigned, however, to an axial  $V^{3+}$  center. In their GaP:V samples Kaufmann *et al.*<sup>14</sup> could not observe any EPR signal that could be ascribed with certainty to  $V^{3+}$ ; the authors argue that the samples were remaining  $n$  type despite V doping, as they could detect the  $Fe^1$  ( $A^-, d^7$ ) signal [thus,  $\mu_F \gtrsim E_v + 2.1$  eV]; we would like to remark that  $V^{3+}$  luminescence can, nevertheless, be excited for these samples.<sup>14</sup> A search for the EPR signal of vanadium in InP:V has proven unsuccessful.<sup>26</sup> In si-GaAs (after illumination) and GaP EPR signals ascribed to the negative charge state of vanadium ( $V^{2+}$ ,  $A^-$ ,  $d^3$ ) were observed by Bates *et al.*<sup>19</sup> through thermally detected (TD) EPR experiments. These data are also included in Table I.

The electrical activity of V centers in these compounds has been the object of much controversy. While it is certainly possible to grow si-GaAs by V doping,<sup>2,3</sup> and Hall-effect measurements<sup>11</sup> would indicate a level at  $\sim E_v + 0.8$  eV in high-resistivity GaAs:V ( $10^8 \Omega \text{ cm}$ ), deep-level opti-

TABLE I. Summary of experimental data for the vanadium impurity in the III-V compounds GaAs, GaP, and InP. Assignments for optical transitions are according to this work. abs, absorption; PL, photoluminescence; ZPL, zero phonon line; max denotes maximum.

		GaAs		GaP		InP			
		V <sup>3+</sup>		V <sup>3+</sup>		V <sup>3+</sup>			
Intra- <i>d</i> optical transitions (eV)	${}^3A_2 \leftarrow {}^3T_2$	0.738	PL-ZPL <sup>a</sup>	${}^3A_2 \leftarrow {}^3T_2$	0.791	PL-ZPL <sup>a</sup>	${}^3A_2 \leftarrow {}^3T_2$	0.705	PL-ZPL <sup>b</sup>
	${}^3A_2 \rightarrow {}^3T_2$	0.79	abs band <sup>c</sup>						
	${}^3A_2 \rightarrow {}^3T_1$	1.009	abs-ZPL <sup>c</sup>	${}^3A_2 \rightarrow {}^3T_1$	1.14	abs max <sup>a,d</sup>	${}^3A_2 \rightarrow {}^3T_1$	0.993	abs-ZPL <sup>c</sup>
	${}^3A_2 \rightarrow {}^3T_1$	~1.1	abs max <sup>a,c</sup>	${}^3A_2 \rightarrow {}^3T_1$	1.756	abs max <sup>d</sup>			
	${}^3A_2 \rightarrow {}^1E$	0.909	(weak) <sup>c</sup>				${}^3A_2 \rightarrow {}^1E$ (?)	1.005	(weak) <sup>c</sup>
	${}^3A_2 \rightarrow {}^1A_1$ (?)	1.335	(weak) <sup>c</sup>				${}^3A_2 \rightarrow {}^1A_1$ (?)	1.292	(weak) <sup>c</sup>
		V <sup>2+</sup>		V <sup>2+</sup>					
	${}^2E \rightarrow {}^2T_1$	0.69	abs <sup>c</sup>	${}^2E \rightarrow {}^2T_1$	similar to GaAs <sup>c</sup>				
	${}^2E \rightarrow {}^2T_1$	1.03	abs (weak) <sup>c</sup>						
Magnetic resonance	V <sup>3+</sup> EPR, <sup>a</sup> ENDOR <sup>c</sup> isotropic V <sup>2+</sup> TD EPR <sup>b</sup>			V <sup>3+</sup> EPR <sup>f</sup> axial V <sup>2+</sup> TD EPR <sup>h</sup>			No signal <sup>g</sup>		
Electrical levels	$E_A(-/0) \simeq E_c - 0.15$ eV <sup>c</sup> $E_D(0/+) \simeq E_v$ <sup>c</sup>			$E_A(-/0) \simeq E_c - 0.8$ eV <sup>c</sup>			$E_A(-/0) \geq E_c$ <sup>c</sup> $E_D(0/+) = E_v + 0.21$ eV <sup>c</sup>		

<sup>a</sup> Reference 14.

<sup>b</sup> Reference 21.

<sup>c</sup> Reference 16.

<sup>d</sup> Reference 23.

<sup>e</sup> Reference 25.

<sup>f</sup> Reference 24.

<sup>g</sup> Reference 26.

<sup>h</sup> Reference 19.

cal spectroscopy (DLOS) experiments<sup>3,13,15</sup> do not show any midgap acceptor level that could be related to the isolated V impurity in GaAs. Litty *et al.*<sup>15</sup> find two levels at  $E_c - 0.14$  eV and  $E_c - 0.23$  eV in *n*-type GaAs, while Brandt *et al.*<sup>17</sup> find just one level at  $E_c - 0.15$  eV. The data of Clerjaud *et al.*<sup>16</sup> and Ulrici *et al.*<sup>18</sup> indicate an acceptor level at  $E_c - 0.14$  eV, and the authors agree that the donor level in GaAs:V should be very close to or within the valence band. Donor action was detected<sup>27</sup> for InP:V with a level at  $E_v + 0.21$  eV, but no acceptor activity. For GaP:V Abagyan *et al.*<sup>23</sup> observe a photoconductivity threshold that could indicate the presence of a deep level, and Clerjaud *et al.*<sup>16</sup> detect luminescence in *n*-type GaP:V that is probably related to the acceptor state ( $V^{2+}$ ,  $A^-$ ,  $d^3$ ). These latter authors suggest an acceptor level at  $\sim E_c - 0.8$  eV, which would be compatible<sup>28</sup> with the acceptor location in GaAs.

We may summarize the data as follows. (i) Vanadium in si-GaAs, si- and moderately *n*-type GaP, and InP presents optical activity characteristic of the neutral state  $A^0$ ,  $T^{3+}$ . (ii) The impurity then presents a high-spin, nonorbitally degenerate ground state, so we do not expect Jahn-Teller effects to be operative; breathing-mode relaxation may occur. (iii) No midgap acceptor level is found by DLOS experiments that can be ascribed to isolated V in si-GaAs, where the acceptor is within 0.2 eV of the conduction band; the location of the acceptor level in GaP is less certain, but it is undoubtedly in the upper third of the band gap; there is no evidence for a V acceptor level in InP, however a V donor is detected at  $E_v + 0.21$  eV. (iv) The data on the preceding item suggest a Mott-Hubbard energy for  $V^{3+}$  of around  $U(A^0, d^2) \simeq 1.4$  eV, similar<sup>4,5</sup> to those of  $Co^{2+}$  and  $Fe^{2+}$  where the *e* orbital is ionized. (v) EPR of isolated (tetrahedral)  $V^{3+}$  was seen with certainty

only for si-GaAs:V; EPR of  $V^{2+}$  was observed in GaP and GaAs, however it is not established the signals are related to the isolated impurity. In the next section we present our results for GaAs:V, and discuss a possible mechanism for the acceptor behavior.

### III. THEORETICAL ANALYSES

#### A. Mean-field MS $X\alpha$ results for the $A^0$ state

We used for GaAs: $V_{Ga}$  a molecular cluster model comprising the central impurity atom, the nearest-neighbor shell of 4 As atoms and the second-neighbor shell of 12 Ga atoms, in the unrelaxed lattice geometry, as used before<sup>7</sup> for other 3*d* impurities. The electronic structure of this cluster is solved, as before, within the multiple-scattering  $X\alpha$  formalism with the Watson-sphere boundary condition. We present our results for the neutral state in Fig. 2.

We can see from Fig. 2 that the impurity introduces an *e*-symmetry level near the middle of the band gap, occupied with two electrons in the neutral charge state  $A^0$ ,  $V^{3+}$ . The antibonding ["dangling-bond hybrid" (DBH)]  $t_2^{DBH}$  level characteristic of 3*d* impurities<sup>4-9</sup> is already in the conduction band, unoccupied in the ground state of the system. The charge localization is very strong for the *e* level, with 70% of the charge within the central muffin-tin sphere (radius 2.45 a.u.), a little more than 5% spread over the first-neighbor shell, and 16% spread over the second-neighbor (Ga atoms) shell. Only 8% of charge is in the interstitial region; the  $t_2^{DBH}$  level is more delocalized, with 32% of charge in the impurity sphere, and 16% spread in the interstitial region. This is the expected

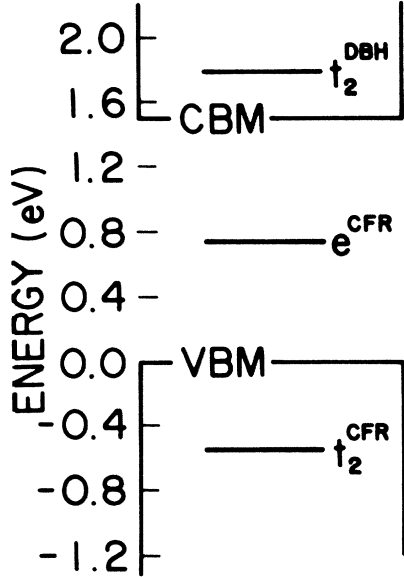


FIG. 2. Mean-field results for the  $d$ -related levels of isolated substitutional vanadium in GaAs, in the neutral ( $A^0, T^{3+}$ ) charge state, with occupation  $e^2t^0$  for the  $e^{CFR}$  and  $t_2^{DBH}$  levels. VBM is the valence-band maximum, CBM is the conduction-band maximum.

behavior<sup>4,5</sup> for the charge distribution of the  $e^{CFR}$  ["crystal-field resonance" (CFR)] and  $t_2^{DBH}$  levels of a  $3d$  impurity [it is to be noted that the charge within the nearest-neighbor cage, or "central cell,"<sup>8</sup> encompasses a larger region, with radius  $\sim 4.9$  a.u. for GaAs]. Within the valence band we have another  $t_2$ -symmetry level  $t_2^{CFR}$  at  $E_v - 0.55$  eV with 43% of charge within the central sphere: this bonding partner of  $t_2^{DBH}$  is fully occupied, and should not affect the electrical or optical properties of the center.<sup>4,5</sup> Optical transitions within the  $V^{3+}$  state (si- or moderately  $n$ -type GaAs) or ionization transitions  $V^{3+} \rightarrow V^{2+}$  should then involve, as for the other impurities Cr to Ni, the two levels  $e^{CFR}$  and  $t_2^{DBH}$ .

### B. Multiplet corrections—optical transitions within the $A^0$ state

We now turn to the analysis of the intra- $d$  transitions observed by absorption or luminescence experiments<sup>3,11–16,18</sup> for GaAs:V. It is well known<sup>4,5,29</sup> that the optical activity is a direct result of the relevance of many-electron multiplet effects, not included in mean-field calculations. One could, in principle, compute the multiplet corrections (MC) to mean-field (MF) theory in the energy of any given term  $\Gamma_i$ :

$$E(\Gamma_i) = E_{MF}^T(m, n) + \delta_{MC}(^{2S+1}\Gamma), \quad (1)$$

where  $E_{MF}^T(m, n)$  is the total mean-field energy of the system in the one-electron configuration  $e^m t^n$  from which the term  $\Gamma_i$  evolves (predominantly). The correction includes term splitting within the configuration  $(m, n)$  and

also interaction within the symmetry (configuration mixing). In the FCZ multiplet scheme<sup>5</sup> we separate explicitly, as in Eq. (1), energies that can be computed by MF theory [which include average electron-electron interactions for the fixed configuration  $(m, n)$ ]. When doing that, we express the multiplet energies in terms of the free-ion Racah parameters  $B_0$  and  $C_0$ , for the proper oxidation state,<sup>30</sup> and the excitation spectrum is obtained through the use of the three internal parameters of the FCZ theory,  $\lambda_e$ ,  $\lambda_t$ , and  $\Delta_{eff}(m', n'; m, n)$ , defined as follows:

$$\Delta_{eff}(m, n; m^0, n^0) = E_{MF}^T(m, n) - E_{MF}^T(m^0, n^0) \quad (2)$$

where  $(m^0, n^0)$  is some reference configuration; the parameters

$$\lambda_e^4 = \frac{\left\langle ee \left| \frac{1}{r_{ij}} \right| ee \right\rangle_{sol}}{\left\langle dd \left| \frac{1}{r_{ij}} \right| dd \right\rangle_{ion}}; \quad \lambda_t^4 = \frac{\left\langle t_2 t_2 \left| \frac{1}{r_{ij}} \right| t_2 t_2 \right\rangle_{sol}}{\left\langle dd \left| \frac{1}{r_{ij}} \right| dd \right\rangle_{ion}} \quad (3)$$

reflect the loss of electron-electron repulsion energy for the  $d$ -shell electrons in the solid, and are related to hybridization with the ligand orbitals.

It should be noted that  $\lambda_e^4, \lambda_t^4$  cannot here be taken as the total  $l=2$  charge within any given radius, as has been assumed in earlier work.<sup>6,7(b)</sup>

Here we did not attempt to calculate  $\Delta_{eff}$ ,  $\lambda_e$ , or  $\lambda_t$  directly from our MF results, but rather took the path of obtaining them from a fit to the experimentally detected optical transitions.<sup>5</sup> Only two strong lines are observed for GaAs: $V^{3+}$  (see Table I), which we take to be the spin-allowed transitions  ${}^3T_2(e^1 t^1) \rightarrow {}^3A_2(e^2)$  in luminescence, and  ${}^3A_2(e^2) \rightarrow {}^3T_1(e^1 t^1)$ . The other spin-allowed transition  ${}^3A_2(e^2) \rightarrow {}^3T_1(t^2)$  is only seen for GaP: $V^{3+}$ . As discussed in the Introduction, we expect that the properties of the systems GaAs: $V^{3+}$  and GaP: $V^{3+}$  will not differ significantly, including the values for  $\Delta_{eff}$ ,  $\lambda_e$ , and  $\lambda_t$ . We further expect  $\lambda_e$  to be the least affected, being related in first approximation to interactions with the second-neighbor shell, while  $\lambda_t$  and particularly  $\Delta_{eff}$  can show more sensitivity to the first-neighbor cage.<sup>4,5</sup> We exploit these characteristics by trying to fit the spectrum for  $V^{3+}$  in GaAs with a set of parameters close to those obtained for GaP. We present in Fig. 3 the multiplet spectra obtained for  $V^{3+}$  in GaAs, GaP, and also InP, along with the experimental lines. The values obtained for the parameters are displayed in Table II.

We used for the transition  ${}^3A_2(e^2) \rightarrow {}^3T_1(e^1 t^1)$  the value of the center of the absorption band, as opposed to the use of the no-phonon line energy. We follow in that the suggestion of Baranowski *et al.*,<sup>29</sup> considering we are not including Jahn-Teller effects.

We note from Fig. 3 that we have a spin-singlet  ${}^1E$  state that could be responsible for the weak line at 0.909 eV in GaAs, although it lies a little too low. We also mention that this is a spin forbidden transition, which might explain the low intensity of the line. The line at 1.335 (Refs. 3 and 16), if related to  $V^{3+}$ , cannot be assigned with certainty to a particular transition.

The ground-state many-electron term  ${}^3A_2$  evolves

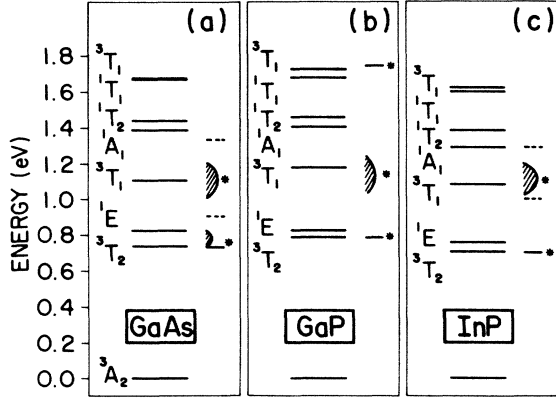


FIG. 3. Multiplet structure obtained for the neutral vanadium impurity ( $V^{3+}$ ) in (a) GaAs, (b) GaP, and (c) InP, from fits to the experimental spectra (to the right of each column). Transition energies used in the fit are marked with an asterisk.

directly from the ground-state mean-field configuration  $e^2t^0$ ; there is no configuration-mixing contribution. It is then a pure  $e$ -character state, and it is thus straightforward to compare the charge distribution obtained here for the (one-electron)  $e^{CFR}$  level with the electron-nuclear double resonance (ENDOR) data of Hage *et al.*<sup>25</sup> as done in Table III. The agreement is excellent, as can be seen from the table, and can be explained (i) by the pure  $e$ -character of the impurity bound state, and (ii) by the extreme degree of localization not only of the impurity-induced perturbation potential, but also of the bound state, which makes the cluster representation very suitable for this particular study.

The values obtained for the parameters (Table II) are very reasonable, in the light of what we would expect for a low- $Z$   $3d$  impurity. We note first that  $\lambda_e > \lambda_t$ , as we would expect from our mean-field results, and also from the behavior of the other  $3d$  impurities.<sup>4,5</sup> On the other hand, we must remember that the recent applications of the FCZ model were all devoted to intra- $d$  transitions within the  $T^{2+}$  oxidation state, and we should expect some different, or “off-trend,” behavior. This feature is manifest in the values obtained for  $\Delta_{eff}$  for  $V^{3+}$ , which are very close to, but *lower* than the values for  $Cr^{2+}$  (also included in Table II). The expected result would be to obtain for  $V^{2+}$  a value of  $\Delta_{eff}$  larger than the value for  $Cr^{2+}$ ; hence we might infer that the effective crystal-field splitting will *increase* with the addition of one electron to the  $d^2$  shell (acceptor state). In the context used here, the ef-

TABLE II. Mean-field parameters for the FCZ multiplet approach, obtained from fits to the experimental data, for the vanadium impurity in GaAs, GaP, and InP. Values for Cr are from Refs. 4 and 5.

		GaAs	GaP	InP
$V^{3+}$	$\lambda_e$	$0.872 \pm 0.006$	0.872	$0.854 \pm 0.006$
	$\lambda_t$	$0.818 \pm 0.006$	0.793	$0.812 \pm 0.006$
	$\Delta_{eff}$ (eV)	$0.60 \pm 0.01$	0.63	$0.60 \pm 0.01$
$Cr^{2+}$	$\lambda_e$	$0.872 \pm 0.08$	$0.872 \pm 0.08$	$0.863 \pm 0.08$
	$\lambda_t$	$0.778 \pm 0.008$	$0.774 \pm 0.08$	$0.790 \pm 0.08$
	$\Delta_{eff}$ (eV)	$0.65 \pm 0.03$	$0.67 \pm 0.03$	$0.64 \pm 0.03$

fective crystal-field splitting measures the average energy required to excite one out of the  $N$  electrons of the  $d^N$  system from the  $e^{CFR}$  to the  $t_2^{DBH}$  level. So, we are proposing an increase in  $\Delta_{eff}$  from  $N=2$  to  $N=3$ , for the same impurity core. A similar system would be the  $d^{10-N}$  shell of octahedral ( $t_2$  below  $e$ ) transition-metal oxides, where we have reliable data on the behavior of  $\Delta_{eff}$  with  $N$ .<sup>31</sup> The equivalent transition to  $V^{3+} \rightarrow V^{2+}$  ( $2 \rightarrow 3$  electrons) in tetrahedral symmetry can be found in the transition  $Ni^{2+} \rightarrow Ni^{3+}$  ( $2 \rightarrow 3$  holes) of NiO; the application of the FCZ model to NiO resulted in  $\Delta_{eff}(Ni^{2+}) \simeq 2\Delta_{eff}(Ni^{3+})$ , or  $\Delta_{eff}(d^{10-3}) \simeq 2\Delta_{eff}(d^{10-2})$ , with very little alteration in the values of  $\lambda_e$  and  $\lambda_t$ .

We do not expect, for an impurity in a covalent semiconductor, that  $\Delta_{eff}$  could be altered quite so drastically, however we think that the value obtained here for the effective crystal-field splitting of  $V^{3+}$  is quite within the expected trend, and that this energy should increase for  $V^{2+}$  in the same compounds [we mention that the value obtained through the MS  $X\alpha$  calculation ( $\sim 1.0$  eV) for  $V^{3+}$  is overestimated, as found for other  $3d$  impurities<sup>7</sup>]. On the other hand, we realize that, due to the stronger impurity-ligand interaction, in a covalent host  $\lambda_e$  and  $\lambda_t$  could be altered from one charge state to another, at least more than in the ionic oxides.

### C. Ionization transitions: acceptor level

Using the data obtained in the preceding section we can estimate the multiplet correction to the acceptor transition. In principle, an ionization transition can involve capture (or emission) of a valence (or conduction) band electron at either the  $\mu=e$  or  $t_2$  impurity levels. The acceptor transition energy where a valence-band (VB) elec-

TABLE III. Charge distribution of the  $e^{CFR}$  impurity orbital of vanadium in GaAs in the neutral charge state ( $V^{3+}$ ), in percents, compared to the ENDOR data of Hage *et al.* (Ref. 25).

Impurity	1st-neighbor shell (As)	2nd-neighbor shell (Ga)	Interstitial region	
70.0	5.3	16.2	8.4	This work
$\sim 70$	7	13		Refs. 4 and 25



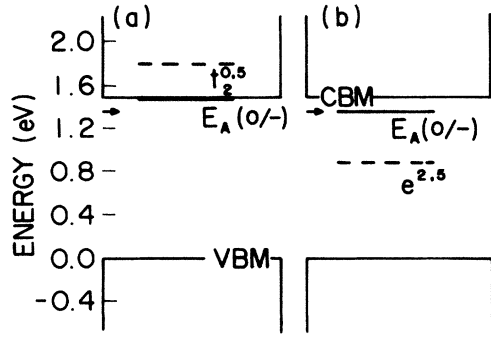


FIG. 5. Different possibilities for the acceptor transition  $V^{3+} \rightarrow V^{2+}$  in GaAs: (a) transition  ${}^3A_2 \rightarrow {}^4T_1$ , capture at the  $t_2$  orbital ( $e^2 \rightarrow e^2 t^1$ ); (b) transition  ${}^3A_2 \rightarrow {}^2E$ , capture at the  $e$  orbital ( $e^2 \rightarrow e^3$ ). Dashed line, transition state one-electron level; solid line, theoretical acceptor level; arrow, experimental acceptor level.

the  $V^{2+}$  center would not be easily detectable, even in  $n$ -type GaAs:V, under normal pressure conditions.

Next we consider, as in Fig. 5(b), the case of a low-spin  ${}^2E(e^3)$  ground state for  $V^{2+}$ . The acceptor level is then at  $E_A(-/0) \simeq E_v + 1.35$  eV, in excellent agreement with the experimental data. The Mott-Hubbard energy  $U(A^0, V^{3+})$  for the neutral center is directly related<sup>5</sup> to the mean-field result for the  $e^{CFR}$  orbital,  $U_{MF}^{ee}$ , plus the multiplet correction

$$\delta_{MC}U = \delta_{MC}({}^2E, e^3) + \delta_{MC}({}^2E, e^1) - 2\delta_{MC}({}^3A_2, e^2).$$

Due to the occurrence of low-spin states at both ends of the transitions, vanadium would be unique in the  $3d$  series in presenting a *sizeable positive correction to  $U$* , of the order of 1 eV. We may mention that, using the calculated value of  $U_{MF}^{ee} \simeq 0.32$  eV, the calculated Mott-Hubbard energy for  $V^{3+}$  is  $U \simeq 1.38$  eV (placing the donor level at the top of the valence band), also in good agreement with the estimated experimental value.

We must remark that lattice relaxation energies were completely neglected in our treatment, and could amount to tenths of an eV. The direction of the change in acceptor levels (either  $e$  or  $t_2$ ), however, would be to higher energies in the gap, as the  $V^{3+}$ ,  ${}^3A_2$  orbital singlet would be subject to stronger breathing mode relaxations.

The net calculated difference in acceptor energies for capture at the  $e^{CFR}$  or  $t_2^{DBH}$  orbitals is only of the order of 0.15 eV, which would perhaps be thought too small to allow a decision to be made based on theoretical results. The ultimate decision as to the final state of the acceptor transition should be given by EPR or ENDOR analyses. Nevertheless, we favor the capture at the  $e^{CFR}$  orbitals, considering (i) the energy level location, (ii) the value for the Mott-Hubbard energy, and (iii) the trend in the values of  $\Delta_{eff}$  for  $T^{2+}$  impurities in III-V compounds.

#### IV. SUMMARY AND CONCLUSIONS

We may summarize the above discussion as follows.

(i) Our mean-field results for GaAs: $V^{3+}$  yield the characteristic level structure of a  $3d$  substitutional impurity in a tetrahedral semiconductor, with a strongly  $d$ -like  $e$ -symmetry level (in the gap, in this case) and a higher-lying  $t_2$ -symmetry level with mixed  $p$ - $d$  contributions; these levels should dominate the excitation and ionization processes. The vertical Mott-Hubbard energy for the  $e$  level amounts to  $U(e^2) \simeq 0.32$  eV, being very small for the  $t_2$  level. The charge distribution for the  $e$  orbital is in remarkably good agreement with the magnetic resonance data for GaAs: $V^{3+}$ .

(ii) Fits to the experimental optical spectra of  $V^{3+}$  in GaAs, GaP, and InP yield the high-spin ground state  ${}^3A_2$  (a pure  $e$  state) for the system, with values for the parameters  $\lambda_e$ ,  $\lambda_t$ , and  $\Delta_{eff}$  in good accord with the general trends observed for other  $3d$  impurities; we consider it very probable that the effective crystal-field splitting will increase in going to  $V^{2+}$ .

(iii) Coupling the results in (i) and (ii), we conclude that the most probable interpretation to the ionization data for GaAs:V is to assume a low-spin ground state ( ${}^2E$ ) for the acceptor ( $A^-, T^{2+}$ ) state, or, in mean-field language, capture and emission at the  $e$  orbital: we have then an acceptor level at  $E_A(-/0) \simeq E_v + 1.35$  eV, and a Mott-Hubbard energy  $U(A^0) \geq 1.38$  eV, which places the donor level very close to the top, or within the valence band.

We conclude, therefore, that any midgap V-related electronic level in GaAs should not be ascribed to the isolated substitutional vanadium impurity, but rather to some complex V-related defect.

More work is still needed, particularly from the experimental side: detailed magnetic resonance experiments on  $V^{2+}$ , for instance, should reflect the similar overall charge distribution of the ground states of the neutral and ionized impurity. Also, detection of the acceptor and donor levels in GaP:V should be possible, as  $U(V^{3+})$  should be mostly transferrable within these III-V compounds; by the same argument, we do not expect the acceptor level to be seen in InP.

*Note added in proof.* Prior to publication, we received a copy of the work by H. K. Yoshida and A. Zunger [Phys. Rev. B (to be published)] on GaAs:V; these authors use a Green's-function technique and include spin-polarization corrections in the mean-field (MF) calculations, hence our MF results are not directly comparable. However, the main conclusions support our predictions.

#### ACKNOWLEDGMENTS

We thank A. Zunger for many fruitful discussions; one of us (S.K.F.) acknowledges support from Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, Brasil).

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