PHYSICAL REVIEW B VOLUME 30, NUMBER 12 15 DECEMBER 1984

Renormalized-defect-molecule approach to the theory of substitutional transition-metal ions in semiconductors

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(Received 18 June 1984)

A theoretical description of substitutional transition-metal ions in semiconductors is presented. It is based on a defect-molecule approach with renormalized parameters in a manner similar to what has been done for vacancies in silicon. The self-consistent calculation allows conciliation of two apparently opposite behaviors: a quasiatomic spectroscopy classically described by crystal-field theory and the stability of several charge states related to the presence of strongly polarizable bonds. The need for going beyond unrestricted Hartree-Fock theory is emphasized and a method for incorporating the effect of Coulomb correlations in the lower configurations is proposed. Multiplet splitting is then calculated for chromium in GaAs and Si, where the excitation spectrum is shown to resemble that predicted by the Tanabe-Sugano diagrams, but with additional excitations from bonding to antibonding states.

I. INTRODUCTION

Among various kinds of point defects in semiconductors, transition-metal impurities are very interesting both from a technological and a fundamental point of view. Their theoretical understanding is still far from complete although there is a wealth of experimental information. A very important aspect is that they tend to remain "quasiatomic" as far as their spectroscopy is concerned, since they are currently described by the well-known crystal-field theory.[1,2] On the other hand, several charge states are observed within the band gap which is evidence of strong coupling to the extended states of the solid. Any physically meaningful theoretical description must then reconcile these two apparently opposite behaviors.

Up to now three types of theoretical approaches have been applied to these impurities: (i) the self-consistent scattered-wave $X\alpha$ method[3,4] first used in this context by Hemstreet[5-8] and extended to interstitial transition-metal impurities in silicon by DeLeo *et al.*[9-11] which treat a small cluster containing the defect, (ii) the pseudopotential local-density calculation performed by Zunger and Lindefelt[12] in a Green's-function formulation, and (iii) the tight-binding work made by Pêcheur and Toussaint[13] again using a Green's-function technique. Treatment (i) can be considered as an approximation of (ii). The three methods require more or less heavy numerical calculation. All provide useful information but with a relatively important error bar as discussed in Ref. 14. They are typically one-electron calculations and only in case (i) have the different authors discussed the influence of correlation effects which are of basic importance for transition-metal impurities.

In this work we want to analyze the problem of substitutional transition-metal impurities from a completely different aspect. The methodology that we use is reminiscent of the one which has proved so successful for the vacancy in silicon for which the (quite precise and abundant) experimental information can be understood in terms of a "defect-molecule model."[15-18] The only difficulty of such an approach lies in the determination of the parameters which take "renormalized" values to account for the interaction between the defect molecule and its environment. We want to work here in exactly the same spirit which allows us not only to get a simple description containing all the essential physical aspects but, as in the vacancy case,[19,20] can be extended to the inclusion of many-electron effects.

We present here a corresponding simple defect-molecule model with three levels of sophistication. In Sec. II we give a restricted Hartree-Fock version which provides a clear illustration of the mechanism discussed first by Haldane and Anderson[21] by which such impurities can give rise to several charge states in the band gap. In Sec. III we show that an unrestricted (or spin-polarized) Hartree-Fock calculation using the same reasonable parameters is bound to give results in contradiction with available experimental data for chromium in GaAs. We demonstrate that this is due to the so called "self-interaction" term and describe in Sec. III how a consistent removal of this term leads to a much more satisfactory picture whose virtue is that it can reconcile both crystal-field and covalency aspects. The set of parameters used throughout this paper has been determined so that the model of Sec. II gives a good fit to experiment. However, as discussed later, there is not much flexibility in their choice, so that our general conclusions do not depend on the details of this choice.

II. EXPERIMENTAL DATA AND SPIN-UNPOLARIZED CALCULATIONS

The experimental energy-level positions determined from techniques such as deep-level transient spectroscopy (DLTS), photoconductivity, etc., include the electron-phonon coupling contradiction. As in the following we derive a purely electronic model (corresponding to nuclei at their perfect-crystal positions) we have to compare the predicted levels to experimental values which are corrected by subtracting the estimated amplitude of the relaxation or distortion contribution. Such corrected electronic energy levels have been determined for the $\mathrm{Cr}^{3+}\rightarrow\mathrm{Cr}^{4+}$, $\mathrm{Cr}^{2+}\rightarrow\mathrm{Cr}^{3+}$, and $\mathrm{Cr}^{+}\rightarrow\mathrm{Cr}^{2+}$ (Refs. 22–24) transitions to lie, respectively, at 0.44, 0.6 ± 0.03, and 1.58 eV above the top of the valence band. Another result we are going to use is the value of 0.82 eV for the internal transition of Cr^{2+} (Ref. 25), which after reduction of the distortion energy gives a purely electronic transition at 0.75 eV. In that case one finds no other states between the $^5T_2$ ground state and ^5E excited state. The final and most important point to note is that all ground states follow Hund's rule.

We first present here a spin-unpolarized model which evidently cannot verify Hund's rule but is the first step in any treatment and will allow comparison with other similar but more sophisticated calculations.[7,12,13] Its main virtue will be to offer a very simple and physically transparent explanation of the mechanism by which several charge states can exist in the band gap, as was first discussed by Haldane and Anderson.[21] For this we use a tight-binding formulation in which use is made of one s and three p orbitals on the bulk atoms, and of one s, three p, and five d orbitals on the transition-metal impurity.

The simplest defect-molecule description is obtained by letting the transition-metal impurity (located at a Ga substitutional site) interact only with the four sp^3 dangling bonds of the first-neighbor arsenic atoms [see Fig. 1(a)]. As in the vacancy case one builds A_1 and T_2 combinations of these dangling bonds whose self-energies are pictured in Fig. 1(b). If we restrict ourselves to "s" and "d" states on the transition-metal impurity these behave, respectively, as basis functions for the A_1 and $E+T_2$ representations. The "s" state will thus couple to the a_1 combination of dangling bonds, while the t_2 "d" states will couple to the corresponding t_2 combinations giving rise to a_1 and t_2 bonding states and a_1^* and t_2^* antibonding states. Only the e-like "d" states will remain uncoupled and will keep their pure atomic character. The corresponding level scheme is described in Fig. 1(b). For neutral chromium (labeled Cr^{3+} in the literature) there are 11 electrons (6 for Cr and 5 for the As dangling bonds) giving rise to the occupancy shown in the same figure.

The important effects arise from the d states so that we concentrate only on the t_2^*,e,t_2 states. Each pair of t_2,t_2^* states is given by diagonalization of a 2×2 matrix of the form

$$\begin{bmatrix} E_d & V \\ V & E_v \end{bmatrix}, \tag{1}$$

where E_d and E_v are, respectively, the energies of the d and t_2 dangling-bond states, while V represents their coupling. In the same simplified scheme, the e-like d states have the energy E_d. The eigenvalues of (1) are

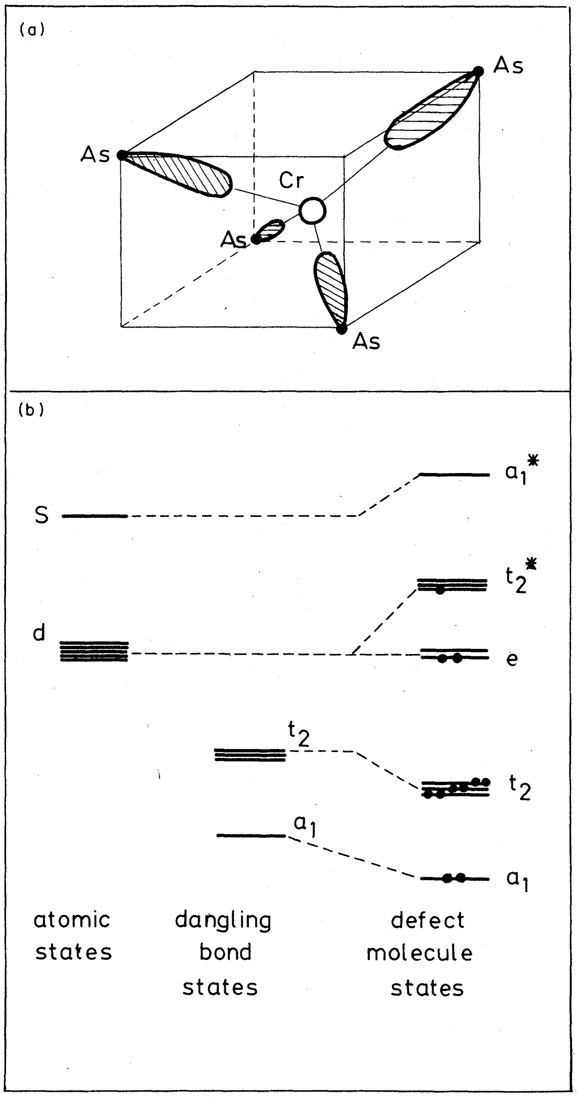

FIG. 1. (a) Chromium interacting with the four sp^3 dangling bonds. (b) Corresponding molecular diagram for neutral chromium Cr^{3+}, the occupancy $t_2^6e^2t_2^*$ is that of the ground state.

$$\epsilon_{t_2}^{t_2^*}=\bar{\epsilon}\pm(\delta^2+V^2)^{1/2}\,, \tag{2}$$

with

$$\bar{\epsilon}=(E_d+E_V)/2\,,$$
$$\delta=(E_d-E_V)/2\,, \tag{3}$$

and the normalized eigenstates are

$$|t_2\rangle=\alpha\,|t_{2d}\rangle+\beta\,|t_{2V}\rangle\,,$$
$$|t_2^*\rangle=\beta\,|t_{2d}\rangle-\alpha\,|t_{2V}\rangle\,, \tag{4}$$

with

$$\alpha^2=\frac{1}{2}\left[1-\frac{\delta}{(\delta^2+V^2)^{1/2}}\right],$$
$$\beta^2=\frac{1}{2}\left[1+\frac{\delta}{(\delta^2+V^2)^{1/2}}\right]. \tag{5}$$

The occupancy of these one-electron levels can be written in the form $t_2^6 e^{n_e}(t_2^*)^{n_A}$ where n_e and n_A vary with the configuration and charge state (n_e+n_A is equal to 3 for neutral chromium Cr^{3+} in GaAs).

To be physically meaningful our description must be self-consistent. This can be achieved by the methods given in Ref. 17, i.e., we write

$$E_d=E_{d0}+\overline{U}(n_d-n_{d0}),$$
$$E_V=E_{V0}+U_V(n_V-n_{V0}), \tag{6}$$

where the numbers of d and dangling-bond electrons are given, respectively, by

$$n_d=n_e+6\alpha^2+n_A\beta^2,$$
$$n_V=6\beta^2+n_A\alpha^2. \tag{7}$$

For Cr in GaAs the natural value for n_{V0} is 3 while for the impurity we consider the d^5s state as the reference state, i.e., we take $n_{d0}=5$ (another choice would simplify shift E_{d0}). With such conventions all the equations above can be condensed into one analytic self-consistency condition with $(2\delta_0=E_{d0}-E_{V0})$

$$\delta=\frac{\delta_0+\frac{1}{2}\overline{U}(n_e-2)+\frac{1}{4}(\overline{U}-U_V)n_A}{1+[\overline{U}+U_V)/(\delta^2+V^2)^{1/2}](6-n_A)}, \tag{8}$$

which can easily be solved by successive iterations.

We now discuss shortly the problem of the numerical values taken by the different parameters. One cannot use parameters corresponding to the free defect molecule, but instead one has to take renormalized values incorporating the effect of the coupling with other atoms. The set of parameters which we use is ($E_{d0}=+2.5$ eV, $E_V=-0.2$ eV, $V=-0.75$ eV, $\overline{U}=8$ eV, $U_V=0.2$ eV, the origin of energies being the top of the valence band). The justification for the choice of such numerical values is given later (see Sec. V). The main point to be underlined is that while the Coulomb parameter $\overline{U}$ on the transition-metal impurity takes a substantial value, the corresponding value of U_V is extremely small. This simply takes account of the fact that when an electron is added on the vacancy states, the level shift is only of order 0.2 eV, i.e., about 50 times smaller than typical atomic values. The mechanism responsible for such a reduction of U_V is described in Ref. 17 and results essentially from delocalization and polarization. We shall see that the small value of U_V is essential for a correct description of the impurity states.

We have solved the self-consistent equations corresponding to four-charge states (Cr^{4+} to Cr^{1+}) for the case $n_e=2$. The results are reported in Table I and Fig. 2. As we can see when we go from Cr^{4+} to Cr^{+}, the electron population in the d shell varies only slightly. The reason for this was discussed first by Haldane and Anderson[21] and then verified numerically by Hemstreet.[8] In our simple description the mechanism becomes transparent: when adding extra electrons these tend to avoid the impurity atom because of the large $\overline{U}$ Coulomb term. This occurs through polarization of the t_2 bonding states by which these electrons are transferred on the dangling-band states (where U_V is small). The polarization mechanism is most efficient when all t_2^* states are empty, i.e., $n_A=0$ as can be verified in Eq. (8) where the term in the denominator contains $6-n_A$. The evolution of the levels with charge state is then considerably reduced with respect to the free atom as can be seen in Fig. 2. This is in agreement with experimental evidence.

TABLE I. Numerical results of the Hartree-Fock calculations. The energies ϵ are referred to the top of the valence band. The parameters used are $\epsilon_V=-0.2$ eV, $U_V=0.2$ eV, $\epsilon_{d0}=2.5$ eV, $\overline{U}=8$ eV, and $V=-0.75$ eV.

	Cr^{+}	Cr^{2+}	Cr^{3+}	Cr^{4+}
$\langle n_d \rangle$	5.14	4.84	4.74	4.68
β^2	0.96	0.79	0.65	0.55
$\epsilon_{t_2^*}$	3.74	1.59	0.98	0.6
ϵ_e	3.58	1.2	0.43	−0.07
ϵ_{t_2}	0.11	−0.25	−0.59	−0.9

It is interesting to compare the predicted levels with those calculated by Hemstreet for Cr^{3+} in GaAs.[7] However, this must be done for the configuration $t_2^6e^3$. The results are given in Fig. 2 and, due to the stabilization mechanism discussed above, are close to those obtained for $t_2^6e^2t_2^*$. The agreement with Hemstreet is good (within 0.2 eV). It is also tempting to compare our predicted lev-

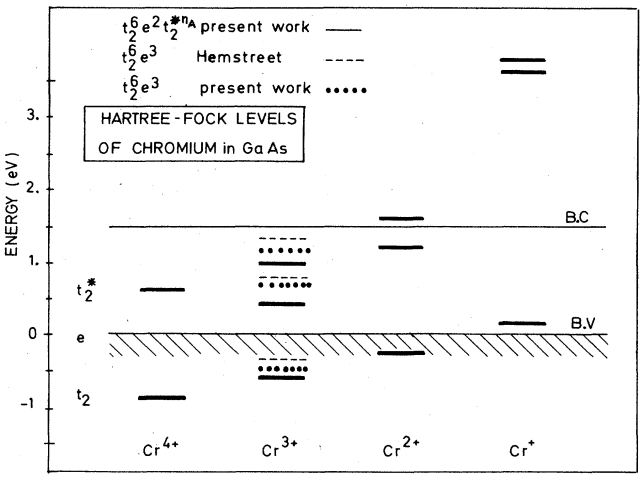

FIG. 2. Hartree-Fock levels of different charge states of chromium. The occupancy is $t_2^6e^2(t_2^*)^{n_A}$; where n_A varies from $n_A=0$ (Cr^{4+}) to $n_A=3$ (Cr^{+}); we also indicate the levels corresponding to our calculation in the configuration $t_2^6e^3$ and compare them with Hemstreet's calculation Ref. 7. The parameters are $\epsilon_V=-0.2$ eV, $U_V=0.2$ eV, $\epsilon_{d0}=2.5$ eV, $\overline{U}=8$ eV, and $V=-0.75$ eV.

els with other calculations, but not for neutral Cr (Cr^{4+}) in silicon. As discussed in Sec. V we modify our parameters simply by shifting ϵ_{V0} by 0.9 eV and rescaling V by using Harrison's rule[26] by which V varies as $d^{-7/2}$ (d, interatomic distance). The results of different calculations are given in Fig. 3. Our calculated levels are in good agreement with those of Hemstreet[5] and Pêcheur and Toussaint[13] but our splittings are 50% smaller than those of Zunger and Lindefelt.[12] The larger disagreement with Ref. 12 is perhaps due to their choice of $X\alpha=1$ which, if it gives a correct gap for GaAs, is not appropriate for the free chromium atom.

The conclusion of this section is that our defect-molecule model (with renormalized parameters) is capable of giving correct energy levels in a spin-unpolarized calculation. It also gives the correct evolution of the levels with charge state. The only thing which obviously it cannot predict is the fact that Hund's rules are satisfied and this must be the subject of a spin-polarized calculation followed by a treatment of multiplet splitting.

III. SPIN-POLARIZED TREATMENTS

A standard method for solving the problem of many-electron effects which are at the origin of Hund's rule is to perform a Hartree-Fock calculation followed by configuration interaction. We shall thus follow first this procedure and present a spin-polarized Hartree-Fock extension of the defect-molecule model presented in Sec. II.

A. Unrestricted Hartree-Fock treatment

We then introduce into the calculation two of the Kanamori parameters,[27] U and J which represent, respectively, the average Coulomb interaction between two electrons in d orbitals and their corresponding average exchange interaction. The d atomic level in the solid now becomes spin dependent and different for the t_2 and e impurity d states. We consider that electrons of a given spin are shared equally between the basis states of the t_2 and e subsets, respectively. With this the t_2 and e atomic levels become distinct and depend upon the spin $\sigma=\pm\frac{1}{2}$ of the electron. The extension of Eq. (6) thus becomes

$$\begin{aligned} E_d(t_2,\sigma)&=E_{d0}+(n_d-n_{d0})U-\left[\frac{U+2J}{3}\right]n_{t\sigma}-Jn_{e\sigma}\,, \\ E_e(t_2,\sigma)&=E_{d0}+(n_d-n_{d0})U-\left[\frac{U+J}{2}\right]n_{e\sigma}-Jn_{t\sigma}\,, \end{aligned} \tag{9}$$

where $n_{t\sigma}$ and $n_{e\sigma}$ are the electron populations of spin σ in the t_2 and e states, respectively.

Now we have to solve two 2×2 matrices like (1) for up and down spin in a self-consistent manner and this, for a given configuration which in our case corresponds to three electrons in each of the $t_{2\uparrow}$ and $t_{2\downarrow}$ bonding orbitals, $n_{e\uparrow}$ and $n_{e\downarrow}$ electrons in each of the $e_\uparrow$ and $e_\downarrow$ orbitals, and, finally, $n_{A\uparrow}$ and $n_{A\downarrow}$ electrons in the $t_{2\uparrow}^*$ and $t_{2\downarrow}^*$ antibonding orbitals. As discussed later we take $U=8$ and $J=0.4$ eV.

Our model is not suited to a calculation of excitation or ionization energies as differences in total energies. To avoid this problem we use Slater's transition-state method, i.e., we calculate these quantities as differences in one-electron eigenvalues in a hypothetical state for which the occupation numbers of the spin orbitals are the averages of those in the initial and final states. Such a procedure is valid to second order in the change of these occupation numbers.

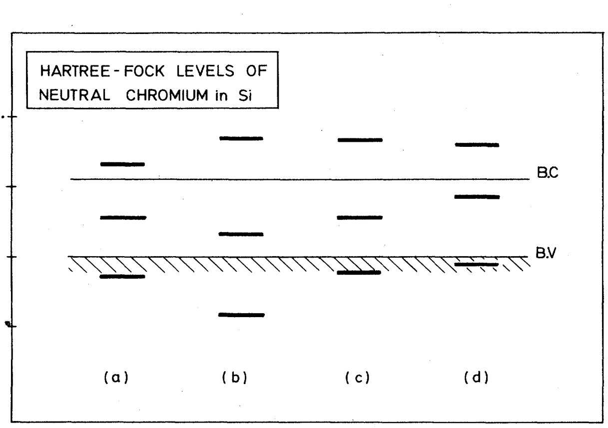

FIG. 3. Hartree-Fock calculation of the neutral chromium levels in silicon: (a) Hemstreet (Ref. 5), (b) Zunger and Lindefelt (Ref. 12), (c) Pêcheur and Toussaint (Ref. 13). (d) Present work with parameters $\epsilon_v=0.7$ eV, $u_V=0.2$ eV, $\epsilon_{d0}=2.5$ eV, $\overline{U}=8$ eV, and $V=-0.85$ eV.

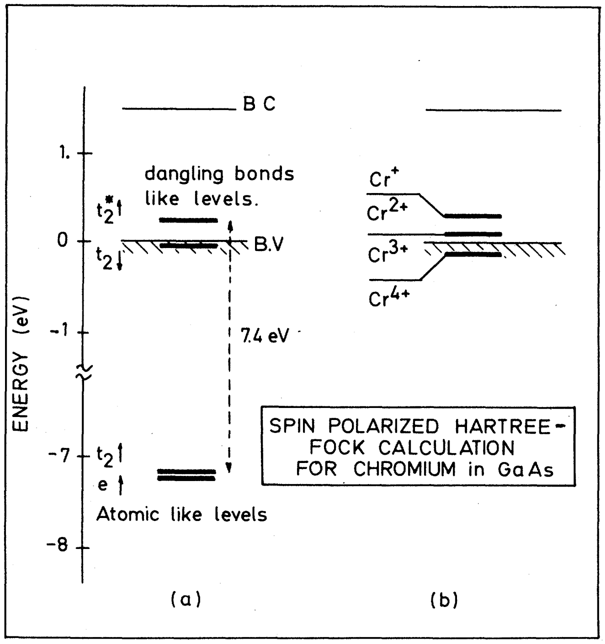

FIG. 4. Spin-polarized Hartree-Fock calculation for chromium in GaAs. (a) Hartree-Fock levels for Cr^{2+}. Note that the $t_2\uparrow$ level is quasiatomic one degenerate with $e\uparrow$, while the $t_2\downarrow$ level is quasi-dangling-bond-like. (b) The three levels in the gap all have a strong dangling-bond character and are thus separated by 0.2 eV, the U_V value of the gallium vacancy. The parameters are the same as in Fig. 2.

Let us begin by discussing the one-electron levels we get for Cr^{2+} in GaAs [Fig. 4(a)] in the configuration $e_{\uparrow}^{2}t_{2\uparrow}^{*2}$ (in the following we do not mention the occupation numbers of the $t_{2\uparrow}$ and $t_{2\downarrow}$ bonding states which are always equal to 3). The striking point is that the $t_{2\uparrow}$ bonding level is very deep and has practically pure d character. As a consequence the $t_{2\uparrow}^{*}$ is dangling-bond-like and close to the valence band. Their energy separation is equal to 7.4 eV, i.e., close to U. In such a case self-consistency is realized mainly with the help of the minority spins (since the $t_{2\downarrow}^{*}$ level is empty).

A consequence of this model is that both $t_{2\downarrow}$ and $t_{2\uparrow}^{*}$ levels are practically dangling-bond-like. Thus if one calculates the ionization energies for different charge states from the eigenvalues in the transition state one finds the results of Fig. 4(b). The partially filled level $t_{2\uparrow}^{*}$ in all cases remains dangling-bond-like in character and its energy is practically pinned. This is at variances with experimental information as discussed in Sec. II. Another important point concerns the ${}^5T_2 \rightarrow {}^5E$ internal transition of Cr^{2+} whose experimental value is 0.75 eV. This transition corresponds, as we shall see later, to an excitation from a configuration $e_{\uparrow}^{2}t_{2\uparrow}^{*2}$ to $e_{\uparrow}^{2}t_{2\uparrow}^{*3}$ corresponding to the energy interval between the $t_{2\uparrow}^{*}$ and $e_{\uparrow}$ levels in the transition state. In this Hartree-Fock model we calculate this energy to be 7.9 eV, which is completely unrealistic.

The cause of such discrepancies is well known and is due to the exchange interaction which is overestimated. This point has been discussed for transition metals[28] and transition-metal oxides.[29] We thus examine now a spin-polarized treatment in which this defect is consistently removed.

B. Improved spin-polarized model

One problem arising in Eq. (9) comes from the averaging procedure which leads to effective exchange terms equal to $(U+2J)/2$ or $(U+J)/2$. In view of the large value taken by U, the energy associated with spin reversal is much too large. As discussed in Refs. 27—29 this energy will be reduced by Coulomb correlations. Hartree-Fock theory fully prevents two electrons of the same spin of being in the same atomic orbital but does not do so for electrons with antiparallel spin. The probability for such situations to occur is thus too large when using the Slater determinantal wave function of the Hartree-Fock approximations. According to the variational principle, correlation effects will act to reduce the statistical weight of these situations. To account for this we shall take the extreme point of view of saying that, when an electron is in one of the atomic "d" orbitals, correlation effects will prevent all other electrons from being in the same orbital regardless of their spin.

In such a scheme the Hartree and exchange part of the d levels can now be written

$$\delta E_{d\sigma} = +U(n_d-1) - J(n_{d\sigma}-1)\,, \tag{10}$$

the same expression holding for all "d" orbitals. We can define the spin polarization in terms of Δn_d,

$$\Delta n_d = \tfrac{1}{2}(n_{d\uparrow}-n_{d\downarrow})\,, \tag{11}$$

and rewrite the d level energy from (10) as

$$\begin{aligned} E_{d\uparrow} &= \bar{E}_{d0} + (U-\tfrac{1}{2}J)(n_d-n_{d0}) - \tfrac{1}{2}J\,\Delta n_d\,, \\ E_{d\downarrow} &= \bar{E}_{d0} + (U-\tfrac{1}{2}J)(n_d-n_{d0}) + \tfrac{1}{2}J\,\Delta n_d\,. \end{aligned} \tag{12}$$

These equations are the direct generalization of Eq. (6) at the condition of replacing E_{d0} by $\bar{E}_{d0}$, U by $U-\frac{1}{2}J$, and by adding an exchange term. We have chosen the parameters in order to get the correct value for the internal transition ${}^5T_2 \rightarrow {}^5E$ of Cr^{2+}. This gives the set of parameters

$$\begin{aligned} &\bar{E}_{d0} = +2.5\ \mathrm{eV}, \quad U-\tfrac{1}{2}J = 8\ \mathrm{eV}\,, \\ &\tfrac{1}{2}J = 0.2\ \mathrm{eV}, \quad U_V = 0.2\ \mathrm{eV}, \quad E_V = -0.2\ \mathrm{eV}\,, \end{aligned} \tag{13}$$

which will be discussed in Sec. V. We now present our results for different charge states of Cr in GaAs and in silicon and compare them to experimental data.

IV. DISCUSSION OF THE RESULTS

The spin-polarized model corresponding to the parameters of Eq. (13) is close to the unpolarized one described in Sec. II. As shown in Table II, it is not surprising that similar behavior is obtained for the dependence with charge state. The only important difference comes from the moderate splitting of the levels with different spin, due to the exchange parameter J. Figure 5 shows this splitting for the levels corresponding to the ground-state configuration of Cr^{2+} in GaAs. One can check that the level ordering and occupation is consistent with the first Hund's rule. We can also see that the splitting of the t_2 state is weak since it has a more pronounced dangling-bond character. Let us now discuss the excitation energies of different charge states of Cr in GaAs.

A. Cr^{4+} in GaAs

In Fig. 6 the excitation energies from the ground-state configuration $e_{\uparrow}^{2}$ to low-lying excited configurations are given. All such energies have been determined using Slater's transition state in our self-consistent spin-

TABLE II. Numerical results of the correlated spin-polarized calculation for chromium in GaAs with the same parameters as Table I and with the additional parameter $J=0.4$ eV. ϵ_I correspond with the ionization energy as experimentally observed but without electron-phonon coupling.

	Cr^{+}	Cr^{2+}	Cr^{3+}	Cr^{4+}
$\langle n_d \rangle$	5.10	4.82	4.74	4.68
$\beta^2\uparrow$	0.90	0.54	0.42	0.36
$\beta^2\downarrow$	0.97	0.88	0.81	0.74
$\epsilon t_2^{*}\downarrow$	4.39	2.17	1.5	1.04
$\epsilon_e\downarrow$	4.25	1.9	1.14	0.6
$\epsilon t_2^{*}\uparrow$	2.54	0.95	0.59	0.33
$\epsilon e\uparrow$	2.30	0.25	−0.3	−0.66
$\epsilon t_2\downarrow$	0.15	−0.14	−0.41	−0.68
$\epsilon t_2\uparrow$	0.03	−0.55	−0.93	−1.23
ϵ_I	1.31	0.74	0.46	−0.89

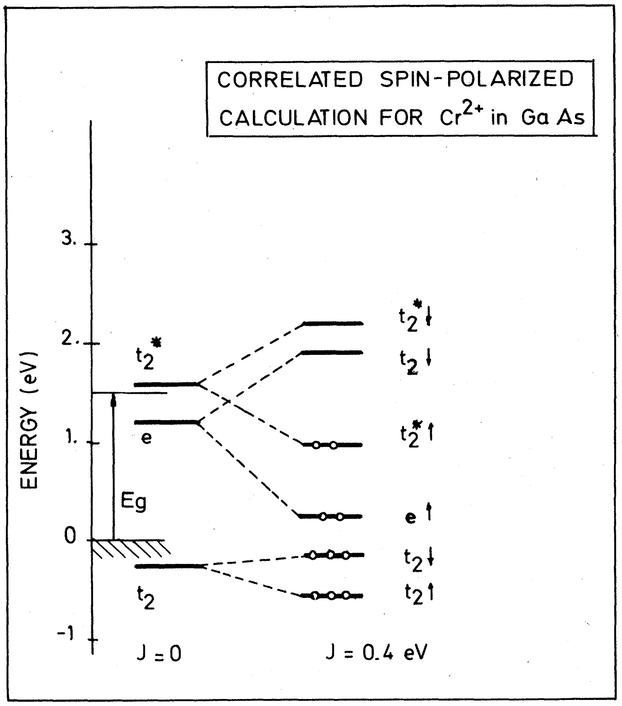

FIG. 5. Lifting of the degeneracy of the Hartree-Fock levels ($J=0$) by our correlated spin-polarized calculation ($J=0.4$ eV) for the $^5T_2$ ground state of Cr^{2+}: ($t_2^6e^2\uparrow t_2^{2*}\uparrow$).

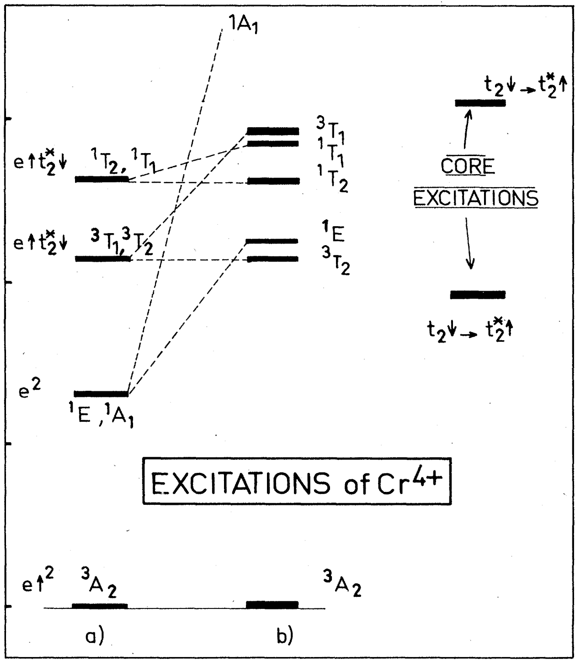

FIG. 6. Internal excitations of Cr^{4+} in GaAs; this spectrum looks like the Tanabe-Sugano diagram but with additional excitations which come from the $t_2\uparrow,\downarrow\rightarrow t_2^*\uparrow,\downarrow$ transitions. (a) States calculated by the "transition-state" method. (b) Lifting of the degeneracy of the previous states by first-order perturbation. The parameters are the same as those given in Fig. 2.

polarized model. Due to our simplified averaging procedure for Coulomb and exchange terms we obtain in several cases an accidental degeneracy. For instance the $e_\uparrow e_\downarrow$ configuration gives rise to two degenerate ^1E and $^1A_1$ levels. We have then calculated the splitting of these two levels by first-order perturbation theory, the perturbation being the difference between more exact Coulomb and exchange parameters and the average ones. This splitting can be expressed in terms of the Racah parameters as described by Griffith[1] for instance. We obtain

$$E(^1A_1)-E(^1E)=\gamma(8B+2C)\,, \tag{14}$$

where B and C are the free atom parameters and γ is a reduction factor (constant for all levels) accounting for solid-state effects (see Sec. V). We have applied the same procedure for all such low-lying configurations and obtained the level structure of Fig. 6.

To our knowledge there are no experimental data on Cr^{4+} in GaAs. Nevertheless, it is interesting to notice that the overall level structure resembles what is obtained from the Tanabe-Sugano diagrams[2] for $Dq/B\sim1.5$. However, there is one important difference coming from what we call core excitations (from the filled shell to the open shell, i.e., $t_{2\uparrow}\rightarrow t_{2\uparrow}^*$) by contrast to the usual ones which occur within the open shell.

B. Cr^{3+} in GaAs

We use the same methodology for neutral Cr in GaAs and obtain the results of Fig. 7. Again the ground state

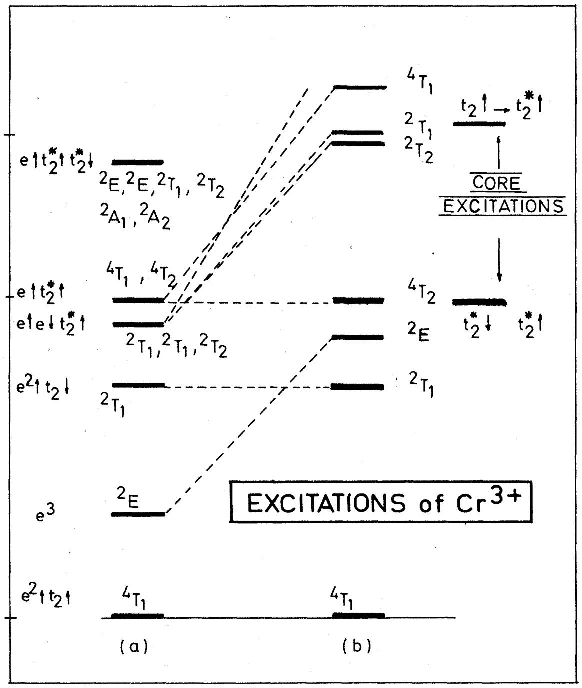

FIG. 7. Internal excitations of Cr^{3+}. The overall characteristics are identical to Cr^{4+}.

obeys Hund's rule and the whole spectrum looks like the Tanabe-Sugano diagrams. However, there is an important difference for the first excited state which we predict to be $^2T_1$. The reason is that the $^4T_1 \rightarrow {}^2T_1$ corresponds to spin flip in the delocalized t_2 orbital. Such a situation cannot be reproduced by standard crystal-field theory.

This charge state has been studied using electron paramagnetic resonance (EPR) by Krebs and Stauss.[30] The ground state $^4T_1$ is strongly coupled with ϵ and τ_2 lattice modes, giving rise to an orthorhombic distortion. Deveaud *et al.*[31] have recently interpreted the optical transition at 0.666 eV as an internal transition $^2E \leftrightarrow {}^4T_1$ at neutral chromium. At first sight Fig. 7 suggests that it might be due to the $^2T_1 \leftrightarrow {}^4T_1$ transition. Both are spin forbidden and a detailed study of the strength of the optical matrix element and Jahn-Teller coupling is needed before any definite conclusion can be reached.

C. Cr^{2+} in GaAs

Our parameters have been adjusted to reproduce the correct $^5E \rightarrow {}^5T_2$ transition. One good test of the validity of our predictions is that we obtain no intermediate states between these two levels (Fig. 8). Hemstreet found such levels[7] but this cannot happen since such levels should open nonradiative channels in such a way that the $^5E \rightarrow {}^5T_2$ could not be observed in luminescence. Another evidence that Fig. 8 should be correct comes from the analysis of the fine structure in the $^5E^*$ state of trigonal $Cr^{2+}-X$, at the origin of the famous 0.839-eV line.[32] The fine structure can be understood in terms of an effective Hamiltonian in the $^5E^*$ excited state:

$$H = \lambda^* \sigma_z S_z + D^* S_z^2 + \mu_1^* \left[(S_Z S^+)_+ + (S_z S^+)_+ \right] + \mu_2^* \left[\sigma^+ (S^+)^2 + \sigma^- (S^-)^2 \right] . \tag{15}$$

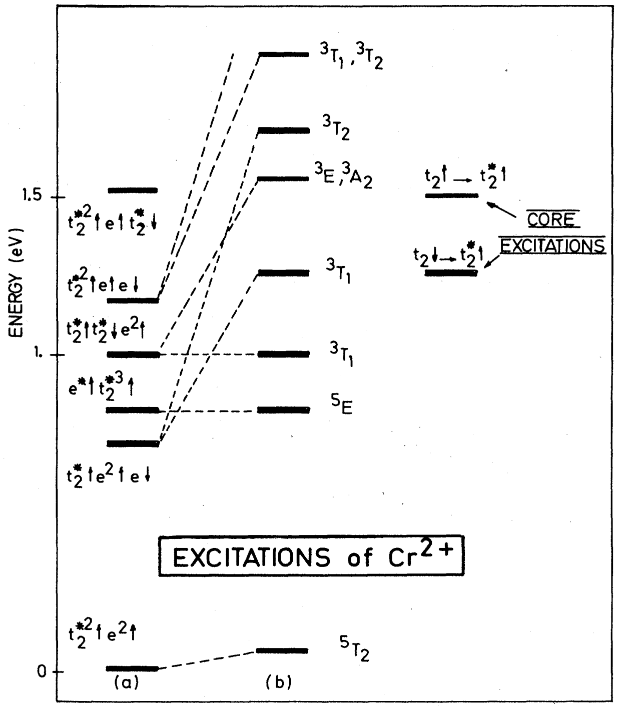

FIG. 8. Internal excitations of Cr^{2+}. Same comments as for Fig. 6.

Uihlein and Eaves[33] have shown that the Zeeman spectroscopy is dominated by the fine structure in the $^5E^*$ excited state with

$$D^* = -0.12 \text{ MeV}, \quad \lambda^* = 0.69 \text{ MeV} . \tag{16}$$

This D^* value cannot be predicted by considering only the spin-orbit coupling between the $^5T_2$ and $^5E^*$ states. One must include other excited states to which coupling can occur via the spin-orbit interaction. Let us assume that such coupling occurs mainly with one excited state. From group theory such a state must be a $^3T_1$ or $^3T_2$ state which in the trigonal coupling will split into two components as shown in Fig. 9. In such a situation one can derive explicit expressions for the parameters defining the effective Hamiltonian of (15). We get the results of Table III (see Ref. 34 for more details). One can see that $^3T_1$ and $^3T_2$ give completely different results, especially as regards the value of μ_1^* and μ_2^*. As discussed in Ref. 34 only $^3T_1$ gives a description coherent with experimental data.

As shown in Fig. 8 our level ordering predicts a $^3T_1$ just above ^5E. This is coherent with the above discussion and shows that, once again, our model gives a completely coherent picture of Cr in GaAs.

To conclude this section it is interesting to see how this model behaves for substitutional chromium in silicon. With respect to GaAs we have to modify only two parameters: the dangling-bond energy E_{V0} and the coupling parameter V. As discussed in Sec. V we estimate V by assuming, as in Harrisson's rules,[26] that it scales like $d^{-7/2}$ from its value in GaAs, i.e., 0.75 eV. As regards the dangling-bond energy it will be shifted upwards to an energy equal to 0.7 eV above the top of the valence band (again see Sec. V for discussion). The corresponding energy levels are given in Fig. 10 for the different charge states. We predict a $Cr^{4+} \rightarrow Cr^{5+}$ level near the top of the

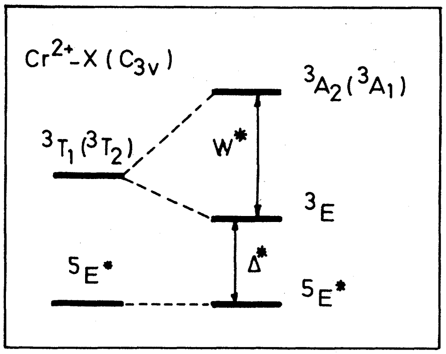

FIG. 9. Selected levels corresponding to the trigonal center $Cr^{2+}-X$ (Ref. 37). In order to explain the fine structure of the first excited state $^5E^*$ we need the proximity of a $^3T_1$ state split by a trigonal field W^*. This state must differ from $^5E^*$ by a monoexcitation in full agreement with what we predict in Fig. 8.

TABLE III. Spin-orbit coupling constant for an effective Hamiltonian acting on a ${}^5E^*$ space by coupling with a split ${}^3T_{1,2}$ state. The effective Hamiltonian is written

$$H=\lambda^*\sigma_Z S_Z+\mu_1^*[\sigma^+(S^+S_Z)_+ +\sigma^+(S^-S_Z)_+]+\mu_2^*(\sigma^+S^{+2}+\sigma^-S^{-2})+(dS_Z^*)^2\,,$$

for more details see Ref. 36. $\langle E\|H_{\text{s.o.}}\|T_{1,2}\rangle$ are the reduced matrix elements. Δ^* are pictured in Fig. 9.

	${}^3T_1$ case	${}^3T_2$ case
λ^*	$3\left[\frac{1}{\Delta^*+W^*}-\frac{1}{\Delta^*}\right]\lvert\langle E\|H_{\text{s.o.}}\|T_1\rangle\rvert^2$	$3\left[\frac{1}{\Delta^*}-\frac{1}{\Delta^*+W^*}\right]\lvert\langle E\|H_{\text{s.o.}}\|T_2\rangle\rvert^2$
d^*	$\left[\frac{1}{\Delta^*+W^*}-\frac{1}{\Delta^*}\right]\lvert\langle E\|H_{\text{s.o.}}\|T_1\rangle\rvert^2$	$\left[\frac{1}{\Delta^*}-\frac{1}{\Delta^*+W^*}\right]\lvert\langle E\|H_{\text{s.o.}}\|T_2\rangle\rvert^2$
μ_1^*	0	$\sqrt{2}\frac{1}{\Delta^*}\lvert\langle E\|H_{\text{s.o.}}\|T_2\rangle\rvert^2$
μ_2^*	0	$\frac{1}{\Delta^*}\lvert\langle E\|H_{\text{s.o.}}\|T_2\rangle\rvert^2$

valence band. The ground state of Cr^{4+} is ${}^3A_2$. To our knowledge there is no experimental indication of any gap level, but EPR gives a signal relative to Cr^{4+}.[35] There is thus good agreement with our predicted level scheme.

The conclusion of this section is that our correlated spin-polarized model is capable of interpreting the existing experimental characteristics of Cr in GaAs but also in Si. Now, we still have to give some justification for the parameters which we have used, although an accurate *a priori* determination of them is not possible at the present time. This shall be the purpose of a future work.

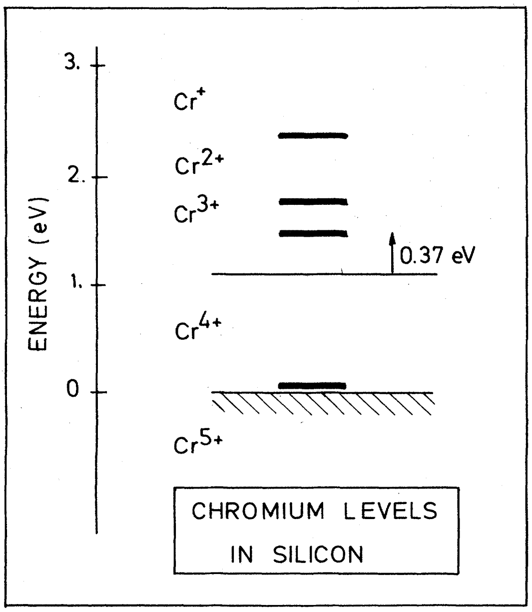

FIG. 10. Level positions for chromium in silicon. The parameters are $\epsilon_V=0.7$ eV, $U_V=0.25$ eV, $\epsilon_{d0}=2.5$ eV, $\bar{U}=8$ eV, and $V=-0.85$ eV.

V. DISCUSSION OF THE PARAMETERS OF THE DEFECT-MOLECULE DESCRIPTION

Before deriving any numerical value for the parameters we have to examine the physical meaning of the defect-molecule concept. The impurity atomic states can be classified with respect to their symmetry ("*s*" or a_1, "*d*" or $e+t_2$). In a tight-binding description we assume that the most important interaction occurs with nearest-neighbors sp^3 orbitals pointing towards the impurity, which we can label sp^3 dangling bonds when the impurity is absent. As is well known these dangling bonds transform as a_1+t_2. In this description the "*e*" states are not coupled which is confirmed by more elaborate calculations. If we now concentrate on the "*d*" t_2 states the corresponding tight-binding matrix takes the form (in a spin-unpolarized scheme)

$$\begin{bmatrix} \underline{H}_{00} & \underline{H}_{0R} \\ \underline{H}_{R0} & \underline{H}_{RR} \end{bmatrix}, \tag{17}$$

where H_{00} is a 2×2 matrix connecting one of the "*d*" t_2 atomic states with the corresponding t_2 combination of the sp^3 nearest-neighbors arsenic dangling bonds. We write it as

$$\underline{H}_{00}=\begin{bmatrix} \epsilon_d & V \\ V & \epsilon_V \end{bmatrix}, \tag{18}$$

where ϵ_d and ϵ_V are the diagonal terms and V is the corresponding hopping integral. This can be viewed as a "bare" defect molecule. Thus H_{0R} and H_{R0} connect this bare molecule with the remaining crystal of Hamiltonian H_{RR}.

Let us now describe how the defect-molecule concept can be used for an accurate description of defect properties. This is based on the concept of an effective Hamiltonian.[36]

We can write the wave function of the system in a basis formed by the atomic state φ_d, the dangling-bond state φ_v, and all other states of crystal. The corresponding coefficients of the expansion will be written as a_d, a_v, and a column vector a_R built from all other coefficients. The equations become

$$\begin{aligned} &(E-\epsilon_d)a_d=-va_v\ ,\\ &(E-\epsilon_v)a_v=-va_d+\underline{H}_{vR}\underline{a}_R\ , \qquad (19)\\ &(E\underline{1}-\underline{H}_{RR})\underline{a}_R=\underline{H}_{Rv}\underline{a}_v\ . \end{aligned}$$

The last equation can be eliminated leading to the 2×2 equations

$$\begin{aligned} &(E-\epsilon_d)a_d=-va_v\ ,\\ &[(E-\epsilon_v)-f(E)]a_v=-va_d\ , \qquad (20)\\ &f(E)=\underline{H}_{vR}(E\underline{1}-\underline{H}_{RR})^{-1}\underline{H}_{Rv}\ . \end{aligned}$$

These equations look like a 2×2 ordinary system except for $\underline{f}(E)$ which is an energy-dependent self-energy term. To recover an effective 2×2 system justifying the defect-molecule concept we first have to normalize the defect-molecule wave function, with

$$a_R=(E\underline{1}-\underline{H}_{RR})^{-1}\underline{H}_{Rv}a_v\ , \qquad (21)$$

$$\begin{aligned} |\underline{a}_R|^2&=\underline{H}_{vR}(E\underline{1}-\underline{H}_{RR})^{-2}\underline{H}_{Rv}|\underline{a}_v|^2\\ &=-f'(E)|a_v|^2\ . \qquad (22) \end{aligned}$$

If we now define

$$a_v'(E)=[1-f'(E)]^{1/2}a_v \qquad (23)$$

we recover the usual normalization condition as

$$|a_d|^2+|a_v'(E)|^2=1\ . \qquad (24)$$

It remains to rewrite the system of equations (20) in terms of a_d and $a_v'(E)$. This gives

$$\begin{aligned} &(E-\epsilon_d)a_d=-\frac{v}{[1-f'(E)]^{1/2}}a_v'(E)\ ,\\ &\left[\frac{E-\epsilon_V-f(E)}{1-f'(E)}\right]a_v'(E)=-\frac{v}{[1-f'(E)]^{1/2}}a_d\ . \end{aligned} \qquad (25)$$

At a given energy E, solution of the problem, this system is now like a 2×2 one with renormalized parameters. To estimate these parameters we notice that, when $v=0$, the second equation of (20) or (25) gives

$$E=\epsilon_V+f(E)\ , \qquad (26)$$

whose solution is E_V, the T_2 vacancy level. From (23) the quantity $1/[1-f'(E_V)]$ represents the value of $|a_v|^2$, i.e., the weight of the sp^3 dangling bonds into the T_2 arsenic vacancy wave function. For energies E in the vicinity of the T_2 vacancy level, i.e., near the energy gap, one can expand $f(E)$ in the second equation (25) near E_V, giving

$$\begin{aligned} \frac{E-\epsilon_V-f(E)}{1-f'(E)}&\sim(E-E_V)\left[\frac{1-f'(E_V)-f''(E_V)\frac{1}{2}(E-E_V)}{1-f'(E_V)-f''(E_V)(E-E_V)}\right]\\ &\sim(E-E_V)\left[1+\frac{f''(E_V)}{1-f'(E_V)}\frac{(E-E_V)}{2}+\cdots\right] \end{aligned} \qquad (27)$$

which, in the first approximation, is equal to $E-E_V$.

This mathematical analysis can be translated in simple physical terms. All happens exactly as if, in the defect-molecule model, the d atomic states were coupled to the sp^3 component of T_2-like As vacancy states. This parameter V of Eq. (1) is equal to $v/[1-f'(E)]^{1/2}$ since $[1-f'(E)]^{-1/2}$ is the amplitude of the vacancy wave function on these sp^3 states. If we calculate v from Harrisson's prescription[26] we directly get $v=1.33$ eV. If we reasonably consider that the weight of the sp^3 states in the T_2 states in the T_2 vacancy state is of order 30% to 40%, then we obtain for V a value close to 0.75 eV, as we have used in the previous section.

The parameter Uv represents the effective Coulomb energy at the vacancy states which we take to be 0.2 eV in agreement with existing estimates.[37] As regards the vacancy level E_V most calculations give a value close to the top of the valence band, i.e., ~ 0 eV,[37] for the neutral vacancy. We chose here $E_V=-0.2$ eV, i.e., take the situation appropriate to the positive gallium vacancy when $n_V=3$ to take into account self-interaction effects.

The three last parameters concern the transition-metal impurity itself. The Coulomb parameter U is, relatively to the Hartree-Fock value, reduced by atomic correlations and solid-state effects but, anyway, the results are not sensitive to this parameter. If we take $U_{\text{atom}}=(\delta E/\delta n)_{n=5}$ we find from experimental value $U_{\text{atom}}=10$ eV which includes atomic correlations effects. In the same way we take, following Ref. 29, $J=\frac{5}{2}B+C$ where B and C are the fitted Racah parameters of the Cr^+ ion, which also contain atomic correlations effects. With $B=0.08$ eV and $C=0.35$ eV (Ref. 1) we obtain $J=0.55$ eV.

We have used for our fit $J=0.4$ eV, so that the agreement is correct if we use a reduction factor $\gamma=0.73$ which is a typical value for the reduction of the Racah parameters of an ion embedded in a solid; this reduction factor is generally interpreted as due to the expansion of the d orbital of the ion when it is incorporated in the solid. So we further reduce $U_{\text{atom}}=10$ eV by the γ factor which gives $\overline{U}=7.3$ eV which is in good agreement with the value used ($\overline{U}=8$ eV).

Finally, an important and difficult parameter to determine is ϵ_{d0}, the "d" level position for $n_d=5$. In principle it might correspond to the "d" free atom level in the configuration d^5s; however in the solid the d shell is not surrounded by an occupied s shell but rather by four dangling bonds which fall in the same space region as the s shell; such overlap effects in general tend to shift the intra-atomic terms upwards with respect to the free atom values. Here we have adjusted ϵ_{d0} to obtain the best overall fit and obtained an absolute value of -3 eV (instead of -10 eV for the free atom) in agreement with the general tendency. A detailed justification of this value is beyond the scope of this paper but would be needed for a systematic extension of the model to other transition-metal ions and semiconductors.

VI. CONCLUSION

We have presented a simple theoretical description of substitutional transition-metal impurities in semiconductors. The corresponding model based on a defect-molecule approach with renormalized parameters is capable of predicting both the defect-ionization energies (gap levels) and the internal transitions. The spectrum of such internal transitions looks like the one predicted by the crystal-field theory (as illustrated by the Tanabe-Sugano diagrams) but with new excitations that correspond to the $t_2 \rightarrow t_2^*$ transitions.

We have found that the charge density in the d shell stays almost constant when the charge state of the defect is changed which is related, as shown by Haldane and Anderson, to the presence of several levels in the gap. In our model the mechanism is quite transparent, consisting of a strong polarization of the t_2 bonding state. The same is true for internal excitations. This strong polarization effect is the essential difference between the present theory and the crystal-field theory where the t_2 bonding states are treated as a frozen core.

In this work we have only treated chromium in GaAs as silicon. The extension to other cases is relatively trivial at the condition of specifying rules for determining the parameters. The basis for such rules has been discussed in Sec. V and further work will be devoted to a systematic study of cases which have been observed experimentally.

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