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Electronic structure of Cu, Ni, Co, and Fe substitutional impurities in gallium arsenide

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We have calculated the electronic structure of neutral copper, nickel, cobalt, and iron impurities replacing gallium atoms in the gallium-arsenide lattice using the $X\alpha$ scattered-wave method. Clusters of 17 atoms in a tetrahedral configuration are used to simulate the bulk and the locally perturbed crystal. The calculations were carried out to self-consistency and in the spin-polarized limit. The results indicate that the impurities studied yield acceptor energy levels deep in the crystal fundamental band gap, in agreement with experiment. The role played by the metal d states in the formation of the impurity centers is discussed and compared with the available experimental data.

I. INTRODUCTION

The study of point defects and impurities in the IV and III-V tetrahedrally coordinated semiconductors has been the subject of many theoretical and experimental investigations.[1-3] While the effective-mass theory[4] has been successfully applied to the study of shallow levels, the theoretical description of the electronic structure of deep impurity levels in semiconductors has challenged the theorists for the last two decades.[5]

Among the large number of theoretical techniques that have been proposed for the study of deep impurities and other localized defects in semiconductors,[6-11] the molecular cluster model rises as a promising approach.[8] The effectiveness of a molecular-orbital treatment of these problems has already been demonstrated by many authors.[12-18] The molecular-cluster model within the framework of the extended Hückel theory (EHT) has been used to carry out electronic structure calculations of substitutional impurities and vacancies in diamond and silicon[12] and vacancies in germanium and gallium arsenide.[13,14] Furthermore, substitutional impurities in diamond, silicon, and germanium have been studied through the molecular-cluster model within the framework of the self-consistent-field-$X\alpha$-multiple-scattering (MS) method.[15,16] This technique was recently applied to calculate the electronic structure of isolated vacancies and $3d$ transition-metal impurities in silicon.[17,18] In this paper the electronic structures of neutral copper, nickel, cobalt, and iron impurities in gallium arsenide are calculated, using the molecular-cluster model within the framework of the MS method.

The interesting electrical, optical, and magnetic properties of gallium arsenide doped with iron-group impurities have motivated many experimental investigations.[19-23] The transition-metal impurities in the lattice can be accommodated either at substitutional or interstitial sites, and give rise to deep local acceptor levels in the forbidden band.[24] However, in spite of the vast amount of experimental data available, there are very few attempts to interpret these data in terms of one of the techniques suited for the deep level problem in semiconductors.[25] In one case a semiempirical Green s-function calculation of the impurity energy levels was performed and the results compared with the experimental observations.[26] Very little theoretical information about the charge distribution associated with the impurity states has been reported until now. Most of the experimental data is interpreted in terms of crystal-field theory, although resonance measurements have shown that spin transfer occurs even for neutral states of these impurities.[21] Hemstreet recently applied the spin-unrestricted-MS method to study chromium-doped gallium arsenide.[27]

The complex interaction between the outer-shell electrons of an iron-group impurity center and the valence electrons of the host-lattice atoms may have contributions from the partly filled d shell of the metal. Most of the experimental results have been interpreted by establishing a correspondence between the different states of the d shell and the deep impurity levels in the band gap. The aim of this work is to establish, for neutral substitutional impurities, the role played by the d shell in the determination of the impurity levels in the band gap.

The results presented in this paper were obtained through the study of a 17-atom cluster employed recently by Fazzio *et al.* to describe the electronic structure of vacancies and substitutional impurities in silicon and gallium arsenide.[28,29] A brief review of the model is given in Sec. II.

II. MOLECULAR-CLUSTER MODEL

The conceptual idea behind the molecular-cluster model for locally perturbed crystals can be traced back to the "defect molecule" model proposed by Coulson and Kearsley.[30] The electronic properties of a point defect in the lattice are determined from the electronic structure of a selected cluster of atoms surrounding the defect. However, as we must be able to locate the impurity level relative to the band edges of the crystal, the bulk solid is simulated by a cluster of host atoms, a "perfect" cluster. A defect in the lattice is then simulated by a "defect cluster", built by suitable modifications of the "perfect" cluster. The cluster electronic structure is studied through a quantum chemistry technique, by imposing appropriate boundary conditions at the cluster surface to simulate the rest of the solid. As far as the covalent solids are concerned, the crucial task is to find the solution for the boundary condition problem. The usual procedure has been to try avoiding the undesirable "dangling bond" effects through the saturation of the surface atoms of the cluster with hydrogen atoms.[12]

In this work the cluster-molecular orbitals (MO) are obtained by solving the one-electron Schrödinger equation within the context of the MS method. The mathematical formulation of the method was extensively discussed in the literature.[31,32] The procedure is self-consistent, therefore the important charge relaxation effects around the impurities are taken into account in the calculations. The standard muffin-tin approximation is assumed for the molecular potential.

According to the model proposed by Fazzio *et al.*,[28,29] the simulation of the rest of the crystal at the cluster boundary is done by first identifying S, the number of electrons in the cluster which correspond to the valence states of the perfect crystal. In a covalent semiconductor S is determined assuming that the chemical bonds between one crystal atom and its four nearest neighbors are saturated by eight electrons, due to the sp^3 hybridization. If N is the total number of valence electrons in the cluster, there will be $N-S$ electrons filling dangling bonds at its surface. These electrons are transferred to a sphere surrounding the cluster (Watson sphere[33]) and are kept fixed throughout the self-consistent calculations. In this way the cluster is electrically neutral, and the bulk band edges are unambiguously determined assuming that the uppermost occupied and lowest unoccupied MO's correspond to the top of the valence band and to the bottom of the conduction band, respectively.

The results reported in this work were obtained from a cluster made of one central atom, 4 nearest neighbors and 12 next-nearest neighbors in a tetrahedral configuration. We are assuming that the impurity atom is in the gallium site of the lattice. It is considered less likely to be on As site because of the greater disparity in size of the atoms. Therefore the "perfect" cluster assumed to represent the ideal crystal is (1 Ga 4 As 12 Ga). This cluster has the central gallium atom and its four-nearest-neighbor atoms completely saturated by $S=32$ electrons in sp^3 chemical bonds. Since $N=59$, we eliminate the "dangling bond" effects by transferring $N-S=27$ electrons to the Watson sphere. The muffin-tin spheres radii, the exchange parameter α, the radius of the Watson sphere, and the size of the partial-wave expansion used in the calculation for this cluster is described elsewhere.[28]

In order to simulate the copper, nickel, cobalt, and iron substitutional impurities in the lattice, "defect" clusters were built replacing the central atom of the "perfect" cluster by the impurity. We assume that the "perfect" cluster with the associated boundary condition provides the "true" crystalline environment for the impurity. The perturbed systems are represented by (4 As 12 Ga + Cu), (4 As 12 Ga + Ni), (4 As 12 Ga + Co), and (4 As 12 Ga + Fe). The exchange parameter α used in the central atom of the "defect" clusters were the corresponding atomic values reported by Schwarz.[34] The interpretation of the calculated results becomes more clear if the energy spectrum associated with a gallium vacancy in the lattice is also considered.[17] In this case the cluster muffin-tin central sphere is empty and the system is represented by (4 As 12 Ga + V). For the vacancy we maintain the value of α used in the perfect cluster. In the central sphere of the "defect" cluster the partial-wave expansion is terminated at $l=2$, where l is the spherical harmonic orbital quantum number.

It is worth mentioning that the "perfect" and "defect" clusters have the same geometrical parameters. Therefore lattice relaxations and distortions are neglected *a priori* in this work.[13,35] Relativistic effects are also not considered.[36] The results are interpreted in terms of the one-particle model, where the spin-polarization effects are taken into account.

III. RESULTS

A. Perfect crystal

The electronic properties of the locally perturbed gallium arsenide are determined by a direct comparison of the electronic structures of the (1 Ga 4 As 12 Ga) cluster and the corresponding "defect" cluster. Therefore we initially show that the main features of the bulk electronic structure emerge from the "perfect" cluster calculation. The self-consistent energy spectra of the cluster (1 Ga 4 As 12 Ga) are presented in Fig. 1. In the 59-electron model all valence electrons are taken into account in the self-consistent calculation. In the 32-electron cluster model, 27 electrons are promoted to the Watson sphere. The energy levels are labeled according to the irreducible representations of the tetrahedral point group Td. Conventional band-structure notations are also utilized to label the relevant band edges. The analysis of the ground-state spectrum of the cluster with 32 electrons enables us to make a clear identification of the bulk states. $3t_2$ is the uppermost occupied energy level and corresponds to the top of the bulk valence band (Γ_{15v}). $3a_1$ is the undermost unoccupied energy level and can be identified as the bottom of the bulk conduction band (Γ_{1c}). $1a_1$ corresponds to the crystal Γ_{1v} energy level. According to the results shown in Fig. 1, the crystal direct band gap and the valence bandwidth are 1.92 and 10.89 eV, respectively. These values agree fairly well with the experimental findings, 1.5 (Ref. 37) and 12.9 eV (Ref. 38), respectively. The energy spectrum of the 59-electron cluster model shown in Fig. 1 is a poor representation of the bulk electronic structure. The "dangling bond" effects lead to a negative value for the crystal band gap. The difference between the model used in this work and that assumed by Cartling[15,16] and Hemstreet[17] is the way the "dangling bonds" are saturated. We point out that for heteronuclear semiconductors, as gallium arsenide, 12 hydrogen atoms may preserve the cluster symmetry but do not saturate the dangling bonds correctly.

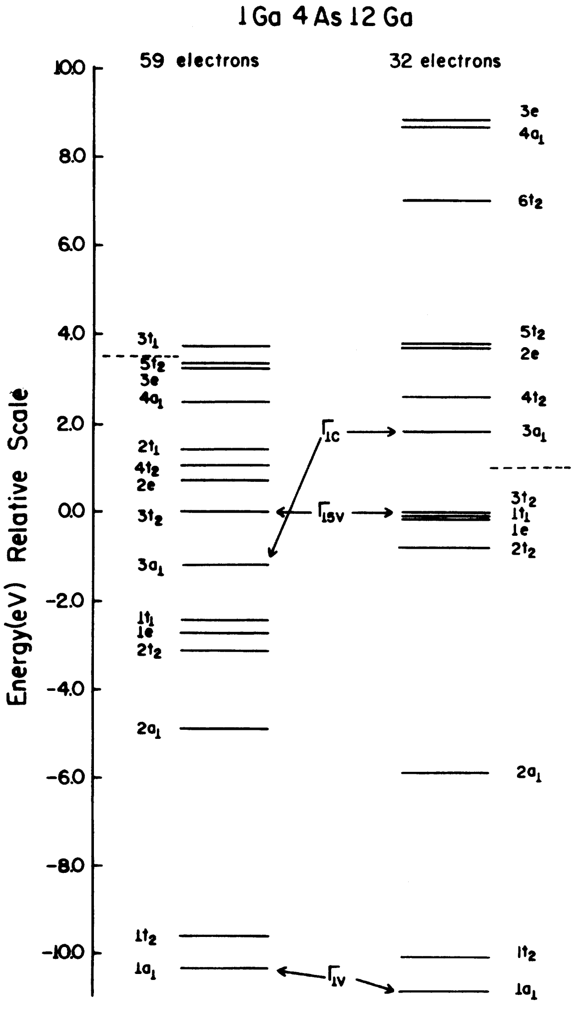

FIG. 1. Energy spectra of the cluster (1 Ga 4 As 12 Ga) used to represent GaAs crystal. The unoccupied energy levels are located above the broken line. The top of the valence band, $3t_2(\Gamma_{15v})$, is placed at the zero of energy. $a_1(\Gamma_{1c})$ is the bottom of the conduction band.

B. Doped gallium arsenide

The manner of defining the energy levels at the center of the crystal Brillouin zone, from the results obtained for the "perfect" cluster, was shown in Sec. II A. For the perturbed systems the band edges will be affected, due to the lower density of states of the small clusters. According to Fig. 1, the levels that define the bulk valence band comprise 2 a_1, $1e$, $1t_1$, and $3t_2$, occupied by 32 electrons. If the cluster central atom is removed to simulate a vacancy, the energy levels with a_2, e, and t_1 symmetries remain virtually unaltered within the one-electron approximation considered here. The s and p atomic orbitals of the central atom do not contribute to MO's of these symmetries. For transition-metal impurities, the d component does contribute to MO's with t_2 and e symmetries. On the other hand, the MO's with a_2 symmetry correspond to high levels in the conduction band. These states are not well described in the cluster model, due to their rather delocalized character in the bulk. Therefore, only t_1 corresponds to a MO which can be identified as a bulk valence state in the "defect" cluster. The related energy level can be taken as a reference to define the band edges of the perturbed systems. The uppermost occupied $1t_1$ level in the cluster corresponds to a nonbonding orbital, as far as the central atom and the nearest-neighbors are concerned. Its charge distribution is the same in all clusters analyzed. This MO is then assumed to be a bulk valence state. When the spin-polarization effects are considered the spin-down energy level ($1t_1\downarrow$) is taken as the reference. Of course, these choices are somewhat arbitrary; however, it is worth mentioning that the conclusions of this work do not change if the cluster energy spectra are compared in terms of absolute scales.

In Fig. 2 the energy spectra of the clusters (1 Ga 4 As 12 Ga), (4 As 12 Ga + Cu), and (4 As 12 Ga + V) are shown, corresponding to the electronic structure of the perfect crystal and the GaAs:Cu and GaAs:V systems. In Fig. 3 we present the results of our study of the GaAs:Cu and GaAs:Ni systems, or the energy spectra of the clusters (4 As 12 Ga + Cu) and (4 As 12 Ga + Ni), respectively. Figure 3 also holds the results for the "perfect" cluster, for comparison. The electronic structure of the systems

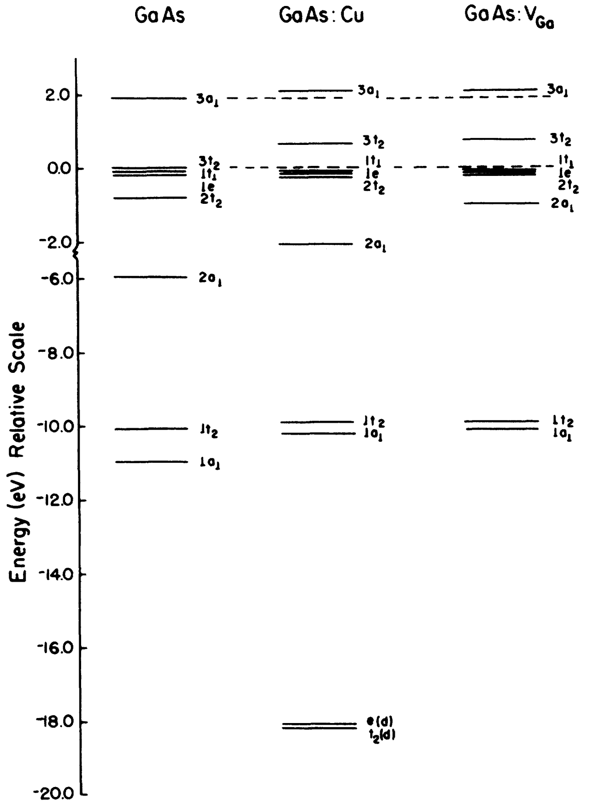

FIG. 2. Energy spectra of the clusters (1 Ga 4 As 12 Ga), (4 As 12 Ga + Cu), and (4 As 12 Ga + V), simulating the electronic structures of the GaAs, GaAs:Cu, and GaAs:V systems, respectively. The dashed lines denote the perfect crystal band gap. The arrows indicate the occupancy of the uppermost occupied levels.

GaAs:Co and GaAs:Fe are compared with those of the bulk in Fig. 4. There we show the energy spectra of the systems (1 Ga 4 As 12 Ga), (4 As 12 Ga + Co), and (4 As 12 Ga + Fe). In all figures the one-electron energy eigenvalues are labeled according to the irreducible representations of the point group *Td*. For the cases where spin-polarized calculations were performed, the energy spectra were separated in *up* and *down* spins. The dashed lines always denote the bulk band gap and were defined from the results obtained for the "perfect" cluster. The uppermost occupied $3t_2$ level in the "perfect" cluster is placed at the zero of energy. The $1t_1\downarrow$ level in the "defect" cluster is placed at the same position that it has in the "perfect" cluster. The occupancies of the relevant energy levels are indicated by arrows (electrons) and circles (holes). All levels below these are fully occupied by electrons.

We start our analysis of the results discussing the interesting features of the energy spectra shown in Fig. 2. When a gallium atom is removed, the $3t_2$ state is no longer at the top of the valence band being

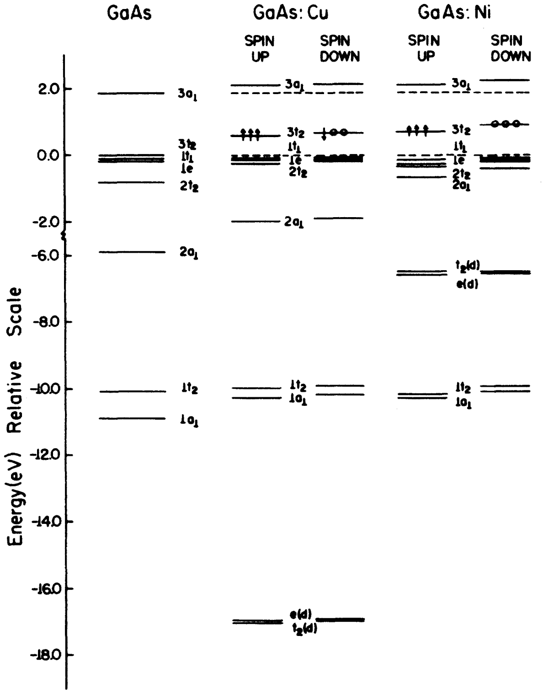

FIG. 3. Spin-polarized one-electron energy spectra of the clusters (1 Ga 4 As 12 Ga), (4 As 12 Ga + Cu), and (4 As 12 Ga + Ni), simulating the electronic structure of the GaAs, GaAs:Cu, and GaAs:Ni systems, respectively. The dashed lines denote the perfect crystal band gap. The arrows (electrons) and circles (holes) indicate the occupancy of the uppermost occupied levels.

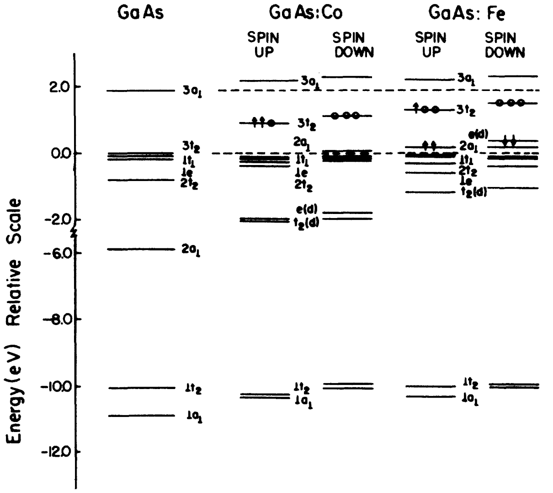

FIG. 4. Spin-polarized one-electron energy spectra of the clusters (1 Ga 4 As 12 Ga), (4 As 12 Ga + Co), and (4 As 12 Ga + Fe), simulating the electronic structure of the GaAs, GaAs:Co, and GaAs:Fe systems, respectively. The dashed lines, arrows, and holes have the same meaning as a Fig. 3.

now introduced into the gap. Since three electrons were removed from the perfect cluster, the vacancy impurity level $3t_2$ has three holes able to accept electrons. The main effect of the creation of the vacancy is the breaking of bonds between the central atom and its neighbors. The $2t_2$ MO, for example, has 20% of its charge inside the central gallium muffin-tin sphere. This charge is reduced to 0.7% when the atom is removed. The same situation is found when copper replaces gallium in the lattice. We observe that the copper d level is located deep in the valence band. It behaves as a core state, interacting weakly with the lattice. A small crystal-field splitting is found, with the sixfold-degenerate $t_2(d)$ level lying below the fourfold-degenerate $e(d)$ level. Since the d states are not able to remake the bonds, the effect of the replacement of gallium by copper in the lattice is the creation of an impurity level $3t_2$ in the band gap, almost at the same position of the vacancy impurity level. Assuming copper in the atomic configuration $3d^{10}\,4s^1$, we conclude that the $3t_2$ impurity level has two holes able to accept electrons. As far as the impurity centers are concerned, the similarities between the energy spectra of the systems GaAs:Cu and GaAs:V shown in Fig. 2 are remarkable.

The comparison of the defect levels associated with the substitutional impurities Cu, Ni, Co, and Fe is done with the results shown in Figs. 3 and 4. All the examinated systems yielded acceptor impurity levels fairly deep in the fundamental band gap. As the atomic number of the metal decreases, the $3t_2$ impurity level rises. These results agree with the non-self-consistent Green's-function (GF) calculation of Ll'in and Masterov.[26] However, these authors report the presence of an unoccupied e level in the band gap, lying above the $3t_2$ level, not found in our calculations. Other discrepancies between the two calculations refer to the impurity levels located close to the top of the valence band. For cobalt the e level enters in the band gap according to GF results, while our calculation leads to an impurity level of a_1 symmetry close to the top of the valence band. For iron our results show that, besides the e level, an impurity level with a_1 symmetry is also found in the band gap. It is interesting to note the behavior of the metal d levels: as the atomic number decreases they rise towards the top of the valence band. From copper to cobalt the d states behave as core states, interacting only weakly with the lattice. Since they are not able to contribute to the formation of a coordination-covalent bond with the nearest-neighbor arsenic atoms, the $3t_2$ impurity level is formed through the same mechanism present in the case of a gallium vacancy. Of course, different impurities represent different perturbations in the lattice, so that the position of the $3t_2$ impurity level is affected. Since the d states are fully occupied, the $3t_2$ impurity levels are acceptors and have two, three, and four holes corresponding to copper, nickel, and cobalt, respectively. Therefore the locally perturbed crystals are open shell systems with the following configurations for the uppermost occupied orbitals: Cu($3t_2\uparrow^3\,3t_2\downarrow^1$), Ni($3t_2\uparrow^3$), and Co($3t_2\uparrow^2$).

In contrast to the situation found for these three impurities, the iron d levels are strongly affected by the tetrahedral crystal field. Although the $t_2(d)$ and $e(d)$ MO's in the spectra of the GaAs:Fe system shown in Fig. 4 have strong contributions from the metal d states, all t_2 in the spectra have admixtures of this atomic orbital. Similarities between the valence MO of the perturbed system and of the perfect crystal are observed. The $4s$ and $3d$ levels in the iron atom are such that s and d orbitals overlap and begin to form the covalent chemical bonding with arsenic atoms. Our results, however, indicate that the remaking of the chemical bonds is not complete. It is important to remark that the energy levels $e(d)\uparrow$ and $e(d)\downarrow$, fully occupied, are introduced in the band gap. GaAs:Fe corresponds to the most covalent system analyzed and is stable in an open shell configuration $3t_2\uparrow^1$.

There are very few studies relating to the charge distribution associated with bound states of substitutional impurities in gallium arsenide. In Table I the charge distributions of clusters expressed in number

TABLE I. Charge distributions of clusters expressed in number of electrons per sphere. For the interatomic and extramolecular regions the total number of electrons is given. The entries refer to the bulk and to the substitutional impurities Cu, Ni, Co, and Fe replacing Ga.

	GaAs	Cu	Ni	Co	Fe
Central atom	30.92[a]	28.93	28.23	27.43	26.25
As sphere	31.60	31.57	31.52	31.47	31.51
Ga sphere	28.52[a]	28.53	28.54	28.54	28.54
Interatomic region	7.53	7.50	7.32	7.25	7.34
Extramolecular region	0.02	0.02	0.02	0.02	0.02

[a] The difference in these values is due to the elimination of the electrons filling dangling bonds in the self-consistent calculation.

TABLE II. Charge distribution normalized to one electron for the bound state $3t_2$ of Ga vacancy and Cu, Ni, Co, and Fe substitutional impurities. This state corresponds to an impurity level located within the crystal direct gap. The charge distribution in the extramolecular region has negligible values.

	$3t_2$(V)	$3t_2$(Cu)	$3t_2$(Ni)[a]	$3t_2$(Co)[a]	$3t_2$(Fe)[a]
Central atom	0.05	0.05	0.05	0.13	0.28
As shell	0.45	0.46	0.44	0.35	0.23
Ga shell	0.25	0.22	0.25	0.29	0.31
Interatomic region	0.25	0.27	0.26	0.23	0.18

[a] From spin-polarized calculations and corresponding to *up* spins.

of electrons per sphere are shown. According to our calculations the number of electrons inside the central muffin-tin sphere for nickel, cobalt, and iron is greater than the corresponding metal atomic number. There is a charge transfer from the arsenic ligands to the metal. For copper, the central sphere encloses 99% of the free-atom total number of electrons. In Table II we show the charge distribution, normalized to one electron, for the impurity bound state $3t_2$ created within the band gap by the vacancy and the impurities. The results emphasize the strong similarity between the impurity bound states formed by the vacancy and copper and nickel impurities. It is interesting to point out that this impurity level results from a perturbation on the state corresponding to the top of the valence band. In fact, the $3t_2$ MO in the "perfect" and in the "defect" clusters have almost the same charge distribution. A significant amount of charge spreads out over the nearest-neighbor shell of arsenic atoms (45%) and a small fraction over the central muffin-tin sphere (5%). This state is more concentrated in the cobalt sphere (12%) and in the iron sphere (30%). The considerable value found for the charge in the iron muffin-tin sphere is due to the participation of the *d* atomic orbitals in the formation of the $3t_2$ impurity state. The charge distributions for the bound state $3t_2$ with spin *down* were not included in the Table II because they are quite similar to those for spin *up*.

A very small crystal-field splitting of the metal *d* levels is observed for copper, nickel, and cobalt. Due to the strong interactions between the *d* states and the tetrahedral crystal field, this splitting is of the order of 1.5 eV for iron. We should remark, however, that the MO's $t_2(d)$ and $e(d)$ in the iron case are not pure *d* states. In fact, for the $t_2(d)$ MO we found contributions from the arsenic *p* orbitals (25%) and from the gallium *s* orbitals (10%). For the $e(d)$ MO the arsenic *p* orbitals and the gallium *s* orbitals also contribute (15 and 20%, respectively).

More insight can be gained concerning the role played by the metal *d* states in the formation of im-

TABLE III. Charge distribution normalized to one electron for the metal *d* states (*up* spins). The charge distribution in the extramolecular region has negligible values.

Impurity	Orbital	Metal atom	As shell	Ga shell	Interatomic region
Cu	$t_2\uparrow(d)$	0.99	0.00	0.00	0.01
	$e\uparrow(d)$	0.99	0.00	0.00	0.01
Ni	$t_2\uparrow(d)$	0.95	0.02	0.00	0.03
	$e\uparrow(d)$	0.98	0.00	0.00	0.02
Co	$t_2\uparrow(d)$	0.83	0.08	0.02	0.07
	$e\uparrow(d)$	0.88	0.04	0.02	0.06
Fe	$t_2\uparrow(d)$	0.57	0.20	0.09	0.14
	$e\uparrow(d)$	0.62	0.10	0.17	0.11

purity centers in gallium arsenide, analyzing the charge distributions for the states $t_2(d)$ and $e(d)$, shown in Table III. The entries correspond to charge normalized to one electron and only values for spin *up* are shown. The metal sphere encloses 99, 95, and 83% of the charge distribution for these MO's corresponding to copper, nickel, and cobalt, respectively. For iron this fraction decreases to 57% for $t_2(d)\uparrow$ and 62% for $e(d)\uparrow$. The remaining charge is almost completely contained in the arsenic shell and in the interatomic region. The $e(d)\uparrow$ impurity level also has 18% of its charge in the next-nearest-neighbor gallium shell.

C. High-spin complex GaAs:Fe

The origin of the deep acceptor states found in transition-metal-doped gallium arsenide is frequently explained in terms of the electronic configuration $3d^n4s^2$ of the metal.[39] The impurity being on substitutional gallium sites is supposed to give two outer $4s$ (one d) electrons to bonding orbitals, leaving a well-localized incomplete $3d^n$ shell. The optical and magnetic properties of those centers are then explained in terms of the crystal-field spectra of the $3d^n$ metal ion. In our molecular-cluster model we fill the MO's in order of increasing energy according to Hund's rule. A strong-field approach is assumed, therefore the formation of low-spin complexes is favored. This assumption seems to be correct for Cu, Ni, and Co impurities, since the d levels are located within the valence band. However, for the GaAs:Fe system there is a possibility that the iron $3d$-shell magnetic moment should persist, when the atom is at the gallium site.[40]

According to the usual interpretation mentioned above, iron replaces a gallium atom in the lattice and contributes three valence electrons to the formation of chemical bonds with the nearest-neighbor arsenic atoms. The remaining five $3d$ electrons form a $^6S_{5/2}$ state and are placed in a weak tetrahedral crystal field. We try to simulate this situation in our model by assuming a spin $S=\frac{5}{2}$ for the open shell system GaAs:Fe. In Fig. 5 we show two self-consistent energy spectra of the system GaAs:Fe, corresponding to the configurations $3t_2\uparrow^1 (S=\frac{1}{2})$ and $1e\uparrow^2\, 3t_2\uparrow^3$ $(S=\frac{5}{2})$. The energy levels labeled $e(d)$ and $t_2(d)$ in the spectrum of the cluster with spin $S=\frac{5}{2}$ also correspond to MO's with strong contributions from d orbitals. The muffin-tin metal sphere encloses 87% of one electron charge for the $e(d)\uparrow$ MO. These fractions are 62, 81, and 71% for $e(d)\downarrow$, $t_2(d)\uparrow$, and $t_2(d)\downarrow$, respectively. The energy levels associated with these MO's are shifted down when the spins are aligned. The $e(d)$ level, which is located within the band gap in the low-spin complex, lies within the valence band in the high-spin complex. The $3t_2$ impurity levels are also shifted down in the high-spin complex, the $3t_2\uparrow$ by about 0.37 eV and the $3t_2\downarrow$ by about 0.01 eV. The $2a_1\downarrow$ impurity level is not affected. Two acceptor impurity levels are introduced in the band gap: a twofold degenerate, $1e\downarrow$, appearing close to the top of the valence band and a threefold degenerate $3t_2\downarrow$ deep in the band gap. Therefore the high-spin system has five holes able to accept electrons.

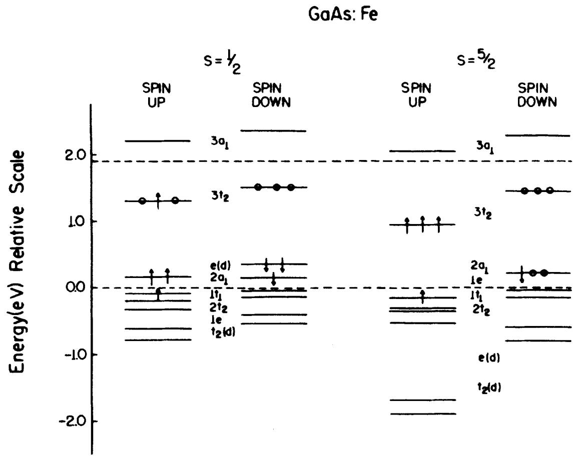

FIG. 5. Spin-polarized one-electron energy spectra of the clusters (1 Ga 4 As 12 Ga) and (4 As 12 Ga + Fe) simulating the electronic structure of the GaAs perfect crystal and iron-doped gallium arsenide. Only details of the gap region are shown. Two configurations of spins were assumed for the ground state of the perturbed crystal, namely $S=\frac{1}{2}$ and $S=\frac{5}{2}$. The dashed lines, arrows and holes have the same meaning as in Fig. 3.

In Table IV we provide details about the structure of the relevant bound states of the GaAs:Fe high-spin complex. Except for $1e\uparrow$, the entries refer to MO's with energies lying within the band gap. The information that emerges from the data shown in Table IV is that the fraction of charge inside the central iron sphere is small for all impurity states. Both $3t_2$ levels have almost the same structure: They are formed mainly from the iron d orbitals, arsenic p orbitals, and gallium s orbitals. The hole impurity state $1e\downarrow$ is the MO with the largest contribution from d orbitals. Even so, arsenic p orbitals and gallium s orbitals contribute to its formation. The energy level $1e\uparrow$ is located close below the top of the valence band and corresponds to a MO with a negligible contribution from iron d states. We remark that the $2a_1\downarrow$, occupied by two electrons, enters the band gap and corresponds to a MO with strong contributions from the arsenic p orbitals.

According to the calculations discussed in this sec-

TABLE IV. Charge distribution normalized to one electron from some bound states of the GaAs:Fe high-spin complex ($S=\frac{5}{2}$). Level occupancies are given in number of electrons per orbital. The entries correspond to impurity states whose energies lie within the band gap, except for $1e\uparrow$.

Orbital (occupancy)	Fe sphere	As shell	Ga shell	Interatomic region	Extramolecular region
$3t_2\uparrow(3)$	0.13	0.34	0.30	0.23	0.003
$3t_2\downarrow(0)$	0.19	0.25	0.35	0.20	0.003
$1e\uparrow(2)$	0.09	0.32	0.35	0.23	0.001
$1e\downarrow(0)$	0.33	0.20	0.29	0.17	0.001

tion the five impurity hole states formed in neutral iron-doped gallium arsenide are not well localized in the $3d$ incomplete shell of the metal. Though they have contributions from the delocalized d states, the arsenic p orbitals and the s and p gallium orbitals enter in their formation.

IV. DISCUSSION

According to our calculations, copper-, nickel-, cobalt-, and iron-doped gallium arsenide yield impurity energy levels fairly deep in the fundamental band gap. Some of them are unoccupied, which explains the acceptor activities detected in these materials.[3] For the GaAs:Cu system the copper d levels are deeply located within the valence band, retaining a corelike character. The impurity level $3t_2$ associated with this impurity has the same structure as the gallium vacancy defect level: it can therefore be associated with the broken bonds at the gallium site. Following the sequence from copper to nickel to cobalt, the d energy levels in the valence band and the $3t_2$ impurity levels in the band gap rise in energy. For the cobalt impurity a small delocalization of the d orbital is observed. These results follow the same qualitative trend as do copper, nickel, and cobalt substitutional impurities in silicon, recently examinated by Hemstreet.[17] The only exception is the GaAs:Co system where an impurity level $2a_1\downarrow$ appears in the gap region, close to the top of the valence band. The $2a_1$ orbital is formed from the gallium $4s$ orbital in the "perfect" cluster, and from the metal $4s$ orbitals in the "defect" clusters. This results in the $2a_1$ levels being progressively dislocated upwards, as the metal atomic number decreases, until the $2a_1\downarrow$ enters the band gap in the case of cobalt and iron.

For iron-doped gallium arsenide ($S=\frac{1}{2}$) the metal d states interact with the nearest-neighbor arsenic atoms and impurity levels, e, with strong contributions from these states are found within the band gap A smaller contribution from these atomic states is found in the impurity level $3t_2$. When the spins are aligned in order to build the high-spin complex ($S=\frac{5}{2}$), the d states become more localized and lead to energy levels located within the valence band. The impurity states $3t_2$ and $1e$ are rather delocalized states, with a significant fraction reaching the next-nearest neighbor shell of gallium atoms. Some similarities can be found between our results for the $S=\frac{1}{2}$ system and those computed by Cartling for iron-doped silicon.[16] The latter seem to indicate that the iron d states participate in a complete remaking of the bonds between the central atom and the silicon neighbors. In the GaAs:Fe system the tetrahedral chemical bonding is partly rebuilt and the impurity levels within the band gap do have contributions from d atomic states.

Before comparing our results with the available experimental data, some comments should be made. Although the self-consistency and the spin polarization are important features of our calculations, we are neglecting the charge relaxation occurring when an impurity level is ionzied. The interelectron coupling that should split the levels into multiplet terms were also not considered.[41] Even so the agreement between our results and the experimental ones is fairly good.

It has been known for a long time that the transition-metal impurities create deep acceptor states in gallium arsenide.[3] Our results seem to explain how these states are formed. One salient feature of the perturbed crystals inferred from the cluster spectra is their possibility of assuming a number of different stable electronic configurations. All the analyzed clusters are open shell systems, where the incomplete shell is formed from the impurity bound states. This explains why transition-metal doping of gallium arsenide usually produces several impurity bands in the luminescence spectrum.[42] Thus, these centers may exist in different ionization states, which hampers a clear interpretation of the electronic transitions in which an impurity is involved. Electron-spin-resonance (EPR) measurements show that the width of the absorption line in gallium arsenide exceeds considerably that of these impurities in ionic compounds.[43] The interesting peculiarity is that the EPR lines are strongly broadened and hard to detect. The iron impurity resonance is easier to detect than the resonances of nickel and cobalt. The EPR signal in copper-doped gallium arsenide was not observed.[21] According to our results the EPR lines have to do with the rather delocalized impurity states. The unpaired electrons of the perturbed crystal spend a considerable time in the neighborhood of the nearest-neighbor arsenic atoms resulting in a hyperfine interaction with the nuclei of the magnetic isotopes. This results in broad spectral lines. In some cases the unpaired electrons even reach the next-nearest-neighbor gallium atoms. The observed EPR lines in gallium arsenide doped with neutral nickel and cobalt seem not to be directly related to the metal d states. Though we have not analyzed the systems GaAs:Ni and GaAs:Co with higher spin configurations, we learned from the GaAs:Fe spectra that the spin alignment lowers the energy of the d states. From the analysis of the electronic structure of iron-doped gallium arsenide in the ^6S state, we may say that the acceptor level $1e\downarrow$ is a deformed iron d function. Recent EPR experiments seem to confirm this fact.[44]

At this point it is well to compare our results with experimental results for the activation energies of the centers under study. The data are shown in Table V. The theoretical values are the direct difference between eigenvalues of impurity states and the top of valence band, neglecting electron relaxation effects. From photoconductivity experiments in GaAs:Cu, s centers located at 0.52 eV and r centers at 0.39 eV, measured from the top of the valence band, are detected.[45] Recently experiments based on the phototrigger effect[22] assigned the position of the r centers at 0.38–0.40 eV, which agrees with the results deduced from the thermal quenching of the intrinsic photocurrent in GaAs:Cu. The s centers are identified as originating from copper impurities and a relationship between the r centers and gallium vacancies has been speculated. Our results for the copper impurity levels are shown in Table V, where we note the presence of two holes within the crystal band gap. According to the energy spectrum of the GaAs:V system shown in Fig. 2, the activation energy of the $3t_2$ acceptor level created by the gallium vacancy is 0.70 eV. This value is in close agreement with the recently reported results, obtained from experiments in the GaAs:V system[46,47]: 0.55, 0.5, and 0.35 eV. It is important to comment on the strong similarity between the GaAs:Cu and GaAs:V systems. An acceptor level with activation energy 0.145 eV is frequently reported for the system GaAs:Cu (Ref. 3); this impurity level was not found in our calculation. Since it is not created by an isolated copper impurity, we may guess that it is due to a complex of copper impurity with another impurity or a vacancy. This hypothesis seems to be reasonable due to the large number of native defects found in the III-V semiconductors.

TABLE V. Impurity levels E within the band gap of gallium arsenide, measured from the top of the valence band.

Theory			Experiment[a]
Impurity	Orbital (occupancy)	E(eV)	E(eV)
Cu	$3t_2\uparrow(3)$	0.60	0.145,[b] 0.39,[c] 0.52[c]
	$3t_2\downarrow(1)$	0.66	
Ni	$3t_2\uparrow(3)$	0.73	0.22,[d] 0.35,[d] 0.44[d]
	$3t_2\downarrow(0)$	0.93	0.53,[d] 0.84,[e] 1.15[e]
Co	$2a_1\downarrow(1)$	0.08	0.14,[d] 0.16, 0.22
	$3t_2\uparrow(2)$	0.97	0.345, 0.54, 0.60[d]
	$3t_2\downarrow(0)$	1.19	0.85–1.10[f]
$\text{Fe}(S=\frac{1}{2})$	$2a_1\downarrow(2)$	0.15	
	$e(d)\uparrow(2)$	0.16	
	$e(d)\downarrow(2)$	0.34	
	$3t_2\uparrow(1)$	1.34	
	$3t_2\uparrow(0)$	1.50	0.22, 0.36, 0.37 0.52, 0.59
$\text{Fe}(S=\frac{5}{2})$	$2a_1\downarrow(1)$	0.22	
	$1e\downarrow(0)$	0.22	
	$3t_2\uparrow(3)$	0.96	
	$3t_2\downarrow(0)$	1.48	

[a] Reference 20.
[b] Reference 3.
[c] Reference 45.
[d] Reference 26.
[e] Reference 49.
[f] Reference 39.

The EPR spectra of nickel-doped gallium arsenide have been obtained by many authors and the data are related with the $3d^7$ and $3d^8$ configurations of the metal.[48] The cluster considered by us to represent this impurity is stable in the spin configuration $S=\frac{3}{2}$, according to Hund's rule. No attempt was made by us to calculate the energy spectra of the systems with higher spins. The activation energies for the centers formed in the GaAs:Ni system have been reported more than ten years ago. Different experimental techniques lead to the values reported in Table V. Most of the data are quoted from Ref. 26. The value 0.84 eV corresponds to a band in the optical-absorption spectra of these materials, observed in recent experiments.[49] It is interpreted as being due to the electronic transition from the valence band to the nickel $3d^7$ level. In the case of strongly compensated samples, the absorption spectra have a second band at 1.15 eV, which is speculated to originate from intracenter transitions in the nickel $3d^8$ configuration.[49] The highest activation energy found in our calculation for nickel was 0.73 eV, and corresponds to a transition from the top of the valence band to the threefold degenerate acceptor $3t_2\downarrow$ level.

Investigations performed on the EPR and magnetic susceptibility of GaAs:Co are usually interpreted taking as a starting point the $3d^6$ and $3d^7$ configurations of the metal.[48] The cluster used by us to simulate the neutral cobalt impurity in gallium arsenide has a spin $S=1$. Three impurity levels are placed within the band gap in this configuration and the values are listed in Table V. There are four holes able to accept electrons within the band gap, corresponding to the $3t_2$ impurity state. Cobalt-doped gallium arsenide has been the object of a great deal of experiments, and activation energies for impurity centers in this material have been reported for a long time. The entries shown in Table V were quoted from Refs. 20, 26, and 39. Recently, data obtained from optical absorption pointed out the presence of three peaks in the spectral region 0.85 to 1.1 eV.[39] They were interpreted according to internal transitions from the ground state Co(d^7) to the three spin-orbit components of one excited state. The center of gravity of this group of peaks is about 0.97 eV. Unfortunately we are not in a position to decide if our calculations are truly comparable with this optical-absorption experiment, since we are neglecting spin-orbit effects. It is interesting, however, to note that a threefold degenerate acceptor level, with activation energy 0.93 eV, is found in our calculations.

Detected EPR in iron-doped gallium arsenide was related to the $3d^5$ configuration of the metal in the ^6S state.[43] The impurity levels obtained by us for low- and high-spin GaAs:Fe are shown in Table V, where we also list the experimental values quoted according to Ref. 20. The highest acceptor level $3t_2\downarrow$ does not change when the spins are aligned. However, significant modifications are observed in the other impurity centers, both in the position of the level and in the character of the impurity bound state. One energy level is removed from the band gap when the spins are paired. Therefore, we point out that by dealing with different configurations or promoting electrons from the valence band to the acceptor levels, many values of activation energies can be expected. The charge relaxations around the impurity due to the activation of the centers deserve further study. Since many experiments deal with compensated samples, it is also useful to obtain the cluster energy spectra when electrons are trapped in the hole states. The cluster model used in this work provides a straightforward tool to study these problems.

Before concluding this work a final comment should be made: It must be specially stressed that the impurity states raised by doping gallium arsenide with copper, nickel, cobalt, and iron are not bound to an isolated impurity. They are bound states of a cluster which contains (besides the metal) the tetrahedron of nearest arsenic atoms and the next-nearest gallium atoms. Although in GaAs:Fe some impurity states have strong contributions from the iron d wave functions, they are rather delocalized in the cluster.

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