Chemistry of Materials 1989, *1*, 587–591

Molecular Cluster Model of the Electronic Structure of Substitutional Impurities in Gallium Arsenide

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Received March 27, 1989

The embedded cluster LCAO-SCC method, within the DV-Xα local density formalism, has been used to investigate the electronic structure of the cation vacancy and of the substitutional Cu impurity in GaAs. The host gap has been found to be 0.8 eV. The pure GaAs and the point defects were represented by $GaAs_4Ga_{12}$, $V^*As_4Ga_{12}$ (V^* = vacancy), and $CuAs_4Ga_{12}$ tetrahedral embedded clusters, respectively. The main features of perturbations induced into the host bonding scheme by point defects are thoroughly discussed. Present calculations predict a Cu acceptor state 30 meV above the valence-band edge, in close agreement with experiments.

Introduction

Semiconductors with different impurities as dopants are of great interest in the production of efficient technological devices like solar cells, microwave devices, and optoelectronic elements.

Shallow impurities[2] introduce minor perturbations in the crystal (actually they give rise to bound states in the fundamental bandgap very close to the band edges) contributing extra charge carriers, electrons, or holes. By far the most important role of shallow donor and acceptor is that of controlling conductivity.[2] On the other hand, if the perturbation induced by impurities or by lattice defects has a more local character, the relative bound states are considerably more localized and often have energies deep in the bandgap. Deep impurities act primarily as carriers traps or recombination centers[2] controlling, as a consequence, the lifetime of charge carriers.

Effective-mass theory furnishes a well-established theoretical framework to explain the microscopic properties and the role played by shallow impurities. In contrast, no such general theory is available for deep impurities, whose electronic structure is investigated by using either a perturbative or a cluster approach.

Perturbative calculations treat impurities as a localized perturbation of the periodic potential (usually described by a Green's function) of the host.[3] In contrast, in the cluster approach, a finite, small number of atoms (the molecular cluster) containing the defect or the impurity is assumed to provide an adequate representation of the crystal region near the defect.[4] Even though the cluster approach is less rigorous than the perturbative one, it provides useful information with lower computational effort, provided that suitable boundary conditions are taken into account.[5–7]

The embedded cluster LCAO-MO method, within the framework of the discrete variational (DV) Xα local density formalism,[8] has been recently applied by Khowash and Ellis[9] in a contribution dealing with the electronic structure of InP, InP:V_{In} and InP:H_{In}. To have a further test about the reliability of this approach in the investigation of the electronic properties of III–V semiconductors, we decided to investigate the electronic structure of GaAs, GaAs:Cu_{Ga} and GaAs:V^*_{Ga} (V^* = vacancy) by using the same method.

Copper is a typical unintentional impurity of GaAs (replacing a Ga atom). Its presence gives rise to two acceptor levels in the material (156 and 450/500 meV).[10] Fazzio and Leite, on the basis of Xα scattered wave (SW) calculations,[11] assigned the acceptor level with higher ionization energy to a simple copper substitution, while they suggested to relate the lower one to a complex of copper with another point defect. On the other hand, Willmann et al. proved that the 156- and the 450-meV levels are to be ascribed to copper center of symmetry C_{3v} and C_{2v}, respectively.[12]

The theoretical results herein reported provide further theoretical information on this matter, suggesting an assignment different from that proposed by Fazzio and Leite.[11]

Theoretical Method

The DV-Xα procedure has been used to determine the wave functions and eigenvalues of an embedded cluster. The rest of the solid is mimicked by providing an electrostatic crystal field and charge field in which the cluster is embedded. This is done by generating a microcrystal surrounding the cluster and placing the atoms at specified lattice positions. A self-consistent procedure is then used to create a Coulomb and exchange-correlation potential

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in which the cluster is immersed. Usually, the microcrystal is chosen to extend to 17–20 au, including in this way 250–300 of the surrounding atoms.

This approach has proved to be very appropriate to investigate systems with defects where the conventional band structure formalism proves intractable or computationally expensive. The crucial point of such a procedure is that of suppressing surface or cluster-size effects by making the peripheral atoms sense a potential similar to that found in the bulk crystal. Moreover, in treating impurity-induced properties where local environment may play a dominant role, representation of the investigated system by a small embedded cluster is not only computationally attractive but also physically reasonable.

The electronic structure calculations used the self-consistent one-electron local density formalism in the Hartree–Fock–Slater (HFS) model. In a nonrelativistic approach, the one-electron Schrödinger equation can be written (in Hartree atomic units, σ represents spin) as

$$H_\sigma \Psi_{i\sigma}(\mathbf{r}) = \epsilon_{i\sigma}\Psi_{i\sigma}(\mathbf{r}) \qquad (1)$$

where

$$H_\sigma = [-\tfrac{1}{2}\nabla^2 + V_{\mathrm{C}}(\mathbf{r}) + V_{\mathrm{XC},\sigma}(\mathbf{r})] \qquad (2)$$

The three terms refer to the kinetic energy, the Coulomb potential, and the exchange-correlation potential, respectively. Here the Coulomb potential includes nuclear and electronic contributions:

$$V_{\mathrm{C}}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\,\mathrm{d}\mathbf{r}' - \sum_\nu \frac{Z_\nu}{|\mathbf{r} - \mathbf{R}_\nu|} \qquad (3)$$

In relation to $V_{\mathrm{XC},\sigma}$ we used the Kohn–Sham–Slater exchange potential[13]

$$V_{\mathrm{XC},\sigma}(\mathbf{r}) = -3\alpha[3\rho_\sigma(\mathbf{r})/4\pi]^{1/3} \qquad (4)$$

where ρ_σ is the density at point $\mathbf{r}$ of electrons with spin σ. Moreover

$$\rho(\mathbf{r}) = \rho_{\mathrm{cluster}}(\mathbf{r}) + \rho_{\mathrm{external}}(\mathbf{r}) = \sum_{i,\sigma} f_{i\sigma}|\Psi_{i\sigma}(\mathbf{r})|^2 + \sum_\nu \rho_{\nu,\mathrm{crystal}} \qquad (5)$$

where $f_{i\sigma}$ are the occupation numbers for the cluster molecular orbitals, and the index ν runs over all the atoms of the crystal not included in the cluster.

The matrix elements of the effective Hamiltonian relative to the one-electron Schrödinger equation are evaluated as discrete sums over a set of pseudorandom points surrounding each atom of the cluster. To calculate the potential by a one-dimensional integration, the actual electron charge density is replaced by a model density:[14]

$$\rho_{\mathrm{cluster}}(\mathbf{r}) \approx \rho_{\mathrm{SCC}}(\mathbf{r}) = \sum_{\nu,n,l} P^\nu_{nl}|R^\nu_{nl}(\mathbf{r}_\nu)|^2 \qquad (6)$$

ρ_{SCC} is a superposition of radial densities centered on the cluster atoms ν, weighted by the Mulliken[15] population P'_{nl} of the orbitals.

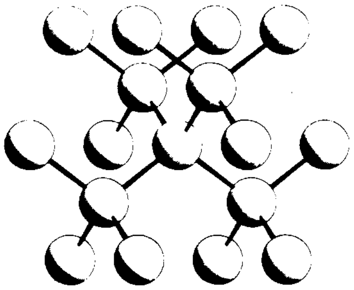

Figure 1. Structure of the $GaAs_4Ga_{12}$ cluster.

Table I. Summary of DV Calculations

cluster size	XAs_4Ga_{12}, where X = Ga, V*, Cu
no. of integr points	6000, pseudorandomly selected
Slater-exchange parameter α	0.70 throughout cluster
potential approx	self-consistent charge model[a]
cell const, Å	5.6533[b]
basis set	nonrelativistic numerical atomic basis
frozen core orbitals	Ga, As: 1s, 2s,2p,3s,3p,3d Cu: 1s, 2s,2p,3s,3p
size of microcryst	276 atoms
cryst pseudopotential	For all points $\mathbf{r}_i < 2.0$ au ($\mathbf{r}_i = |\mathbf{r} - \mathbf{R}_i|$, where $\mathbf{R}_i$ is the position of an ion external to the cluster) the potential V is truncated to −0.20 a.u.

[a] From ref 13. [b] From ref 9.

The Coulomb potential from each spherically symmetric charge distribution is given by the one-dimensional integral:

$$V^i_{\mathrm{C}}(r) = 4\pi\left[\frac{1}{r}\int_0^r \rho(r')r'^2\,\mathrm{d}r' + \int_r^\infty \frac{\rho(r')}{r'}r'^2\,\mathrm{d}r'\right] - \frac{Z_i}{r} \qquad (7)$$

The total nonspherical Coulomb potential is the sum of all the spherically symmetric contributions from all the atoms of the microcrystal; in our case, this was done by means of a generalized Ewald-type summation.[16]

A pseudopotential was used on crystal atoms to simulate Pauli exclusion effects and thus prevents the deep potential field from draining charge from the cluster. Since the clusters investigated in the present contribution are not stoichiometric, charge transfer produces some small electronic flow to or from the cluster. We have chosen to renormalize valence occupation numbers in the $GaAs_4Ga_{12}$ cluster to guarantee a neutral unit cell.

Results of Calculations

When discussing the electronic states of impurities in semiconductors, it is often useful to think of impurity formation as a two-step procedure: creation of a host vacancy (V*), followed by placement of the impurity atom at the V* site.

The above-described cluster embedded procedure has been used to compute Mulliken populations, one-electron energies, and density of states (DOS) for the pure GaAs and for the $GaAs{:}V^*_{Ga}$ and $GaAs{:}Cu_{Ga}$ systems in their neutral (A^0) charge states. The tetrahedral cluster, consisting of 17 atoms (the "perfect cluster" $GaAs_4Ga_{12}$; see Figure 1), used as a model for bulk GaAs contains three symmetry-related sets of atoms: the central gallium atom, a shell of 4 neighbor arsenic atoms, and a shell of next-

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Table II. Atomic Character from the Cluster Embedded SCC DV-Xα Calculation of $GaAs_4Ga_{12}$[a]

	Ga		As		
MO	4s	4p	4s	4p	assgnt
$2t_1$	9	52	0	39	P_I
$5t_2$	4	52	0	44	
2e	14	48	0	38	
$4t_2$	17	45	1	37	
$3a_1$	52	25	13	10	P_{II}
$3t_2$	68	13	8	11	
$1t_1$	9	52	0	39	
1e	79	2	0	19	
$2t_2$	81	3	0	16	
$2a_1$	70	0	29	1	
$1t_2$	17	9	74	0	P_{III}
$1a_1$	27	5	67	1	

[a] Only occupied levels are reported.

neighbor 12 peripheral gallium atoms (hereafter Ga_p). The potentials of the two types of Ga atoms were averaged toghether. Removing of such a constraint introduces only minor variations in the results.

The clusters representative of the defects (the "defect clusters") have been obtained by replacing the central Ga atom either with V* or Cu; then, they have been embedded into the frozen electrostatic crystal field and charge field self-consistently obtained for the "perfect cluster".

Details of the DV-Xα calculations are reported in Table I. The numerical atomic bases, obtained for the neutral atoms, were computed in a potential well 2 Ry deep, having an internal and external radius equal to 4.0 and 6.0 au, respectively. To include functional freedom for the V* site, a 1s basis function for a $Z = 0$ nucleus has been also generated. The absence of the attractive nucleus necessitated a well 20 Ry deep up to 3 au, rising to 0.0 Ry at 25 au, according to previously published procedure.[17] The DV-Xα self-consistent cluster energy levels have been broadened by a Lorentzian of fixed width to simulate a continuous DOS.[18] It is worth mentioning that the "perfect" and "defect" clusters have the same geometrical parameters. Therefore, lattice relaxations and distortions are neglected in this work, even though some aspects of these effects will be qualitatively discussed. Moreover, keeping in mind that neglecting multielectron effects in the investigated systems does not lead to severe errors,[19] we are confident that our mean-field approach is sufficiently adequate.

Electronic Structure of the Host. The first problem to be solved has been the choice of the correct number of electrons to be used to fill the DV-Xα self-consistent cluster energy levels. In principle, any number of electrons between 59 (the neutral cluster) and 32 (the ionic extreme) would be correct.[7]

In this regard, it is worth mentioning that the computed charges for constitutive atoms are usually considerably less than the relative oxidation numbers. On the basis, we decided to use the smallest cluster charge (3+) consistent with a closed-shell system, i.e., 56 electrons according to previous calculations on the isoelectronic InP.[9]

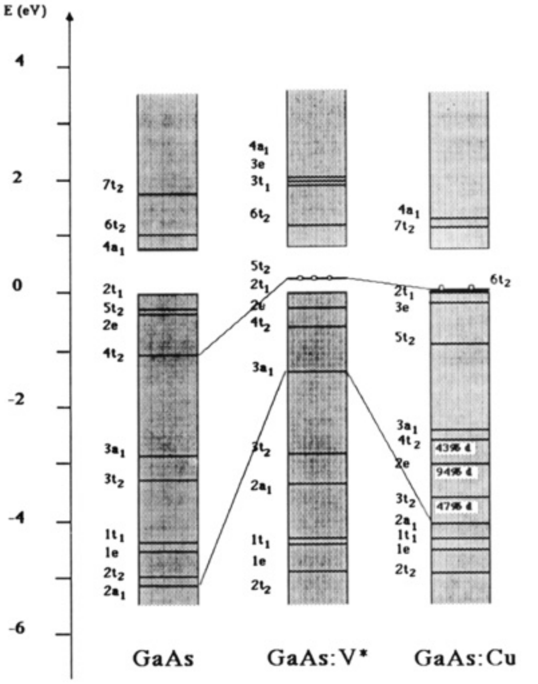

Figure 2. Self-consistent one-electron energy spectrum of GaAs, GaAs:V*, GaAs:Cu. The $2t_1$ levels of the different clusters have been aligned and assumed as the valence-band edge (see text). Open circles represent the hole occupancy of the gap levels.

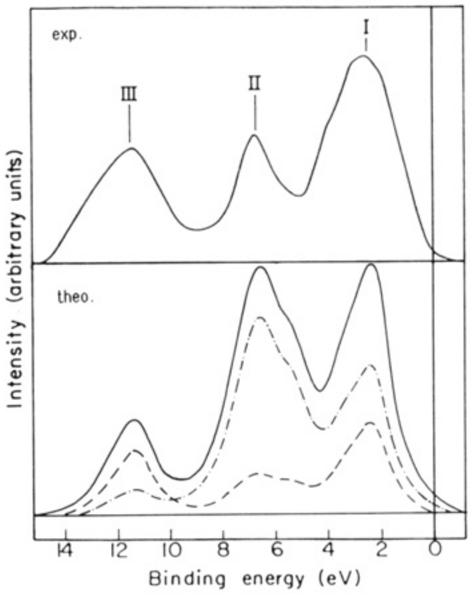

Figure 3. Comparison of the valence-band X-ray photoemission spectrum of the GaAs crystal (from ref 20) with the valence DOS of the $GaAs_4Ga_{12}$ cluster (full line); the dashed and dashed-dotted lines correspond to the partial DOS of arsenic and gallium atoms, respectively.

The computed spectrum of the one-electron eigenvalues is shown in Figure 2, while in Table II the relative charge density analysis is reported. The highest occupied molecular orbital (HOMO) $2t_1$ and the lowest unoccupied MO (LUMO) $4a_1$ represent the valence-band and the conduction-band edges, respectively. Their energy difference, 0.8 eV, can be assumed as the fundamental bandgap energy. The discrepancy with the experimental value (1.5 eV)[10] is not surprising, since it is a well-known consequence of the local exchange-correlation potential approximation.[9] Our eigenvalue spectrum agrees quite well with those already published by Fazzio and Leite[11] and by Hemstreet,[20] with the exception of the energy region between ≈-5 and -1 eV containing, in the present case, the MOs mainly localized on the 4s atomic orbitals (AOs) (see Figure 2 and Table II) of the Ga_p.

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Table III. Mulliken Population Analysis for GaAs, GaAs:V^*_{Ga}, and GaAs:Cu_{Ga}

	GAs_4-Ga_{12}		V^*As_4-Ga_{12}		$CuAs_4$-Ga_{12}
Ga					
4s	1.81		1.86		1.86
4p	0.83		0.83		0.82
net charge	+0.36		+0.31		+0.32
As					
4s	1.84		1.90		1.87
4p	3.54		3.24		3.41
net charge	−0.38		−0.14		−0.28
				Cu	
		V* 1s	0.11	3d	9.77
				4s	0.60
				4p	0.41
		net charge	−0.11	net charge	+0.21

In Figure 3 the valence-band X-ray photoemission spectrum of the GaAs perfect crystal[21] is compared with the computed total valence DOS. A common feature of the experimental valence DOS of tetrahedrally coordinated binary semiconductors is the presence of three well-defined peaks (P_I, P_{II}, P_{III} in Figure 3). These peaks derive from the outermost cation and anion s and p electrons. The charge-density analysis (see Table II) indicates that 4s As AOs strongly contribute to the peak P_{III}, while 4s Ga AOs significantly participate in the peak P_{II}. Finally, both Ga and As 4p AOs are involved in peak P_I. As a whole, the agreement between the valence-band X-ray photoemission spectrum of the GaAs perfect crystal[21] and the computed total valence DOS is satisfactory (see Figure 3). Both the nonstoichiometricity of the investigated cluster and the difference in the energy dependence of the partial photoionization cross section, relative to the various valence bands, result in variation in amplitudes between the observed and calculated peaks.

Electronic Structure of the Defects. The one-electron eigenvalues obtained for the defect clusters $V^*As_4Ga_{12}$ and $CuAs_4Ga_{12}$ are reported in Figure 2. The spectra has been shifted in energy in order to align the $2t_1$ levels. Actually, these levels can be assumed as a reference because the corresponding MOs are virtually unmodified in the investigated clusters (no orbital of the central atom can contribute to them).

The main effect of the vacancy creation is the breaking of the four bonds ($a_1 + t_2$ in the T_d symmetry) between the central gallium and the four neighbor arsenic atoms. As a consequence, the $2a_1$ and $4t_2$ levels of the $GaAs_4Ga_{12}$ cluster (the MOs mainly responsible for the Ga–As σ interaction; see Figure 4) undergo a dramatic shift toward higher energy, giving rise to the fully occupied $3a_1$ and to the half-occupied $5t_2$ levels (three electrons must be subtracted from the cluster because of the removal of the neutral gallium atom). The $5t_2$ MO can be thought as a simple acceptor-state 250 meV above the valence-band edge. Moreover, making reference to the orbital occupation numbers (see Table III), we see that the ionic charge of Ga and As is reduced with respect to that of the "perfect cluster". In particular, a charge transfer to V* (it is an acceptor with 0.11e excess) from the As neighbors is present. This is consistent with the trend showed by the total Ga_p–As overlap population (OP) (0.591e in GaAs, 0.573e in GaAs:V*). Once more the present results are virtually identical with those obtained by Fazzio and Leite[11] and by Hemstreet,[20] apart from differences already stressed in relation to the "perfect cluster".

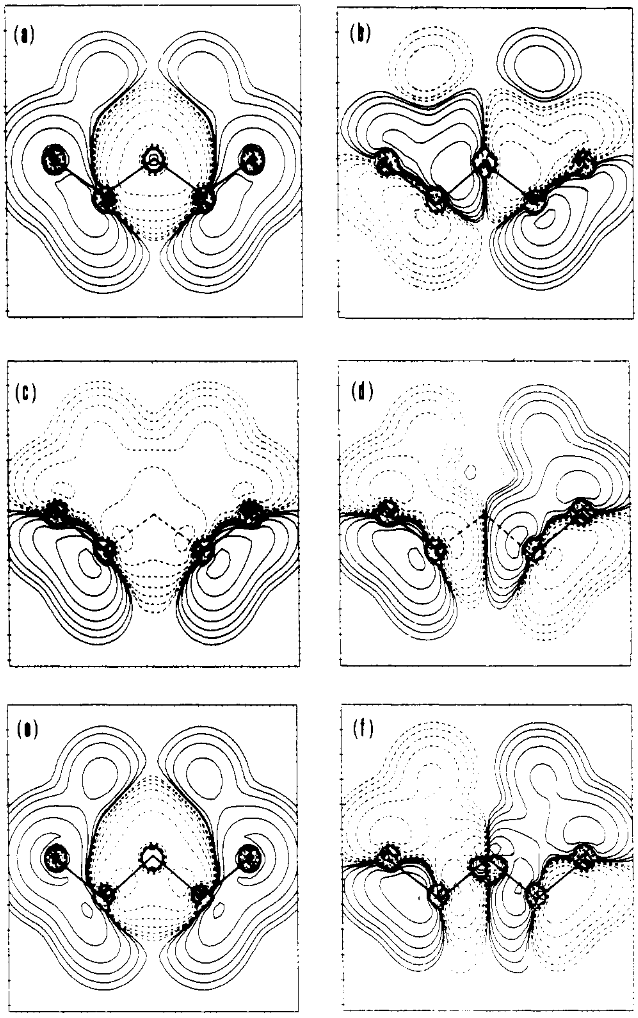

Figure 4. DV–Xα contour plots of $2a_1$ (a), $4t_2$ (b) of the $GaAs_4Ga_{12}$ cluster; $3a_1$ (c), $5t_2$ (d) MOS of the $V^*As_4Ga_{12}$ cluster; $2a_1$ (e), $5t_2$ (f) MOS of the $CuAs_4Ga_{12}$ cluster. All the maps are in the (110) plane; logarithmic contour levels are $\pm 8 \times 10^{-4}$, $\pm 16 \times 10^{-4}$, $\pm 32 \times 10^{-4}$, ... $e^{1/2}/Å^{3/2}$.

The second step in the procedure is that of placing a neutral copper atom (with 11 valence electrons) at the vacancy site, raising the total number of electrons from 53 to 64. Copper 3d levels lie well deep in energy into the valence band (see Figure 2), mostly localized into the resonances $3t_2$ (47% $3d_{Cu}$), 2e (94% $3d_{Cu}$), and $4t_2$ (43% $3d_{Cu}$). Their energy position, which agrees well with that computed by Hemstreet,[20] allows them to strongly interact with the $3t_2$ level of the "perfect cluster", significantly localized on the Ga_p atoms.[22] The presence of such an interaction was not revealed in earlier cluster calculations[11,20] because of either the smaller cluster size or the smaller variational space. Moreover, it confirms that the significative physical extension of the perturbations induced by the point defect is not limited to the impurity nearest neighbors.

The $6t_2$ MO of the GaAs:Cu system is strongly reminiscent (see Figure 4) of the GaAs:V* $5t_2$ level because of its poor energy matching with the Cu 3d orbitals. As a consequence, the t_2 contribution to the Cu–As interaction is very low (the total Cu–As OP t_2 in symmetry is 0.098e). Nevertheless, the picture of an isolated copper atom at the

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[22] At variance with Fazzio and Leite[11] a non-core-like character is obtained for 3d Cu AOs. Incidentally, they computed the 3d Cu levels at ≈−18 eV.[11]

gallium vacancy site is not completely correct because of the strong a_1 σ interaction between the diffuse Cu 4s AO and the suitable combination of 4p As AOs (the total Cu–As (Ga–As) OP a_1 in symmetry is 0.170e (0.157e)).

According to the energy spectrum of GaAs:Cu system reported in Figure 2, the ionization energy of the $6t_2$ acceptor state is 30 meV. More accurate calculations, including spin polarization and application of transition-state procedure, did not modify this value.

Two acceptor levels are measured for GaAs:Cu (156 and 450 meV, labeled C and F, respectively).[12] Fazzio and Leite assigned the F acceptor level to a simple neutral copper substitutional on the basis of their Xα–SW cluster calculations,[11] which predicted a Cu acceptor level at 600 meV. Moreover, they proposed to associate the C level to a complex of copper with another point defect. The energy position of the $6t_2$ MO in our calculations would suggest an opposite assignment. At this regard, it is worthwhile to mention that Hemstreet computed a Cu acceptor level at 380 meV.[20]

From an experimental point of view, Willmann et al.[12] proved, through photoluminescence measurements, that C and F acceptor levels are related to neutral copper centers of C_{3v} and C_{2v} symmetry, respectively. Such a result excludes a simple nature for the F acceptor but does not exclude it for the C acceptor. Actually, the $(t_2)^4$ electronic configuration of the GaAs:Cu system will undergo a trigonal Jahn–Teller distortion.[23] As a consequence, the $6t_2$ MO will be split into a stabilized e state (fully occupied) plus an empty, destabilized a_1 state. Hole emission from the a_1 MO to the valence-band edge determines the acceptor level. Therefore, we argue that the inclusion of lattice distortion effects in the presence calculations would give an even better agreement with the experimental result, even though a C_{3v} complex defect $Cu_{Ga}V^*_{As}$ cannot be ruled out.

Conclusions

We have carried out detailed electronic structure calculations of cation vacancy and Cu substitutional impurity in GaAs, by using the cluster embedded DV-LCAO-SCC Xα method. The combined use of the cluster embedded and DV-Xα procedures allowed a more accurate description of the impurity–host interaction with respect to previous cluster calculations.

GaAs and the point defects were represented by $GaAs_4Ga_{12}$, $V^*As_4Ga_{12}$, and $CuAs_4Ga_{12}$ tetrahedral clusters, respectively. Both the computed intrinsic bandgap and the valence density of states relative to the host are in fair agreement with experiments and previous theoretical results. The vacancy creation gives rise to an acceptor state ($5t_2$ MO) 250 meV above the valence-band edge. Moreover, Mulliken population analysis indicates that the ionic charge of Ga and As atoms is reduced on passing from the $GaAs_4Ga_{12}$ to $V^*As_4Ga_{12}$ cluster. In particular, a charge transfer to V* from the As neighbors is present, with a concomitant decreasing of the bonding interaction between As and Ga_p atoms. The electronic structure of the GaAs:Cu bandgap energy region has been found, according to other cluster calculations, to be very similar to that of the cation vacancy. However, the 3d Cu AOs were not found to be corelike, and actually they significantly interact with suitable levels of Ga_p atoms.

A t_2 level, 30 meV above the valence-band edge, has been found in calculations relative to $CuAs_4Ga_{12}$. Such a simple copper substitutional impurity level has been assigned to the 156-meV acceptor level due to a neutral copper center of C_{3v} symmetry. Neglecting of lattice distortion effects should not invalidate our conclusions. Actually, we argue that the inclusion of lattice distortions in the present calculations would give an even better agreement with experiments.

Acknowledgment. Thanks are due to F. De Zuane for his technical assistance.

Registry No. GaAs, 1303-00-0; Cu, 7440-50-8.

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