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Relationship between donor defects and band structure in III-V alloys

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We examine the correlation between the existence of deep donor levels (*DX* centers) in III-V alloys and the nature of their band structure. Experiments show that the energy position of the *DX* level is directly related to that of the *L* or *X* valleys of the conduction band, irrespective of the nature of the impurity and of the lattice site it occupies. We conclude that the intervalley mixing plays a key role in driving the donor ground state deep. We then reexamine the relevance of the cavity model, which is commonly used to treat the intervalley mixing in the effective-mass approximation. We find that the cavity model contains unphysical ingredients that make it irrelevant to any study of donor impurities. A different model is proposed that involves a donor pseudopotential finite everywhere. Within this model, the *DX* center in $Ga_xAl_{1-x}As$ corresponds to a central-cell correction of standard magnitude (0.6 eV), leading to a deep ground state located 0.2 eV below the *L* extrema of the conduction band, while all the excited states are shallow. This pseudopotential model with central-cell correction in the multivalley effective-mass Hamiltonian is able to account for the main observed characteristics of the *DX* center.

I. INTRODUCTION

In semiconductors, *n*-type doping with substitutional simple donor impurities introduce shallow energy levels close to the bottom of the conduction band, which can be described within the effective-mass approximation (EMA). Usually, the ground state is slightly deeper than expected, and this is ascribed to a so-called central-cell correction. However, in some cases this ground level is rather deep into the gap, typically at few hundreds of meV below the bottom of the conduction band. In that case, we call this donor defect a *DX* center as a natural generalization of the definition of the *DX* center in $Ga_{1-x}Al_xAs$.[1] In such alloys, there is strong evidence that the rather deep *DX* level is directly related to the isolated substitutional donor (for a recent review on the properties of the *DX* center, see Ref. 2). In addition to a relatively deep ground state, which exists for an alloy composition *x* larger than ~ 0.2, one observes shallow excited states as well.[3]

Although extensively studied, the origin of the ground state of the *DX* center is not understood and its atomic configuration unknown.[4] This is due to the dual nature of this center which makes the use of the classical approximations to investigate its electronic structure impossible: the EMA may well describe the shallow excited states but not the deep ground state. On the other hand, the deep ground state suggests a localized description in terms of Green-function supercell techniques in the local-density approximation which, however, is not relevant for the shallow excited states.[5]

The aim of this work is to examine in detail the correlation between the existence of the *DX* center in III-V alloys and the nature of the conduction-band structure. For this purpose, we investigate the existence of the *DX* center in the III-V semiconducting alloys, whose band structures are reasonably known as a function of the alloy composition *x*, namely $Ga_{1-x}Al_xAs$, $As_{1-x}P_xGa$, $In_{1-x}Ga_xP$, $In_{1-x}Al_xAs$, $Ga_{1-x}Al_xSb$, $As_{1-x}P_xIn$, $In_{1-x}Ga_xSb$, $Ga_{1-x}In_xAs$, $Sb_{1-x}As_xGa$, and $In_{1-x}Al_xP$. The results (see Sec. II) give evidence that the *DX* center is present and manifests itself as a deep level E_T located at 150–200 meV below the *X* or the *L* conduction-band edge, provided this location places this level in the forbidden gap (i.e., does not interfere with conduction states issued from the Γ valley). We shall see that this result supports our previous model[6] according to which the existence of the *DX* center is a consequence of the nature of the band structure, and takes its origin in intervalley mixing.

One can wonder why we come back to the question of the nature of the *DX* center when it seems now widely accepted that it is the donor impurity *D* which undergoes a large lattice distortion by trapping an extra electron, i.e., by becoming a D^- state exhibiting a negative-*U* behavior.[5] This model is only suggested since the type of calculations on which it is based can only provide qualitative trends, as illustrated by the fact that similar calculations[7] provided more recently an opposite result (namely that the D^+ state is stable while the D^- is metastable). The experimental evidence which supports this model is mainly based on the observation by electron paramagnetic resonance (EPR) and related techniques. The nonobservation by EPR of the *DX* ground state is said to be the proof that this state is nonparamagnetic, i.e., not D^0, although shallow donor states are similarly not detected in Ge. Many other indications, too numerous to be cited here, are also presented as argument in favor of the negative-*U* model. But they are apparently not convincing enough since additional arguments continue to appear. Recently, a spectrum associated with the Sn impurity in Sn-doped $Ga_{1-x}Al_xAs$ has been detected under photoexcitation at low temperature.[8] With this spectrum exhibiting a hyperfine interaction, it is concluded that the *DX* center must have a strongly localized wave function. However, the materials in which such observation is made contain a Sn concentration 40 times larger than the detected spin concentration [as revealed (yet unpublished) by secondary-ion mass spectroscopy], and the observed spectrum can well be associated with a Sn related defect and not with substitutional Sn on Ga sites. Moreover, this spectrum does not exhibit the so-called persistent photoconductivity (PPC) effect (i.e., it decays even at 4 K when the photoexcitation is shut off), while this PPC effect is the typical characteristics of the *DX* center detected in case of Sn-doped materials by deep-level transient spectroscopy (DLTS). Finally, the experimental evidence for the identification of a *DX* center as a D^- state is thus still weak, and even in contradiction with the existence of a very shallow stable D^- state which has been recently detected.[9,10]

Here we shall not discuss the negative- or positive-*U* character of the *DX* center. We will be dealing with the physical reason for the localized nature of this center. We intend to show that the more or less localized character of the *DX* center is a consequence of the nature of the band structure. That this localization leads to a negative electron-electron interaction is another problem beyond the scope of this paper.

II. EXISTENCE OF THE *DX* CENTER IN III-V ALLOYS

The band structures of the alloys mentioned in the Introduction are displayed in Figs. 1(a)–1(h). The criterion we propose to be fulfilled in order for the *DX* center to exist is the following. In $Ga_{1-x}Al_xAs$, the *DX* level is located at an energy about 150–200 meV below the *L* valley of the conduction band. Moreover, this energy is little affected by the nature of the donor impurity and its lattice site: experimentally, within the experimental accuracy, the *DX* energy level appears to be the same[11] for a given *x* value for whatever the nature of the impurity and the lattice site it occupies. Therefore, we expect this location to be very similar in all alloys, which exhibit comparable effective masses. We thus predict that the *DX* center will exist, provided a level at about 200 meV below the *X* or *L* valleys of the conduction band falls in the energy gap. The approximate ranges of alloy compositions for which this condition is fulfilled are listed in Table I and the conduction-band structures sketched in Fig. 1.

1. $Ga_{1-x}Al_xAs$. Since the criteria used to predict the existence of the *DX* center are derived from the observations of the *DX* center in $Ga_{1-x}Al_xAs$ alloys, there is of course a one-to-one correspondence between prediction and observation. For $x>0.2$ [Fig. 1(b)] the ground *DX* level is a deep level at about 150–200 meV below the *L* valleys.[11–13] At first sight, one might also envision a *DX* level, higher in energy than the ground state, at 200 meV below the *X* valleys of the conduction band, since such a level would also fall in the gap. We shall see, however, in Sec. III that two such levels cannot coexist. Only the ground level remains deep. The basic reason for this is that the upper level must be orthogonal to the ground state. Like in any orthogonalized plane-wave band calculation, this orthogonalization to the core state amounts to a repulsive central-cell correction to the effective potential, so that the upper state is forced to be shallow.

2. $GaAs_{1-x}P_x$. The *DX* center is also present undoubtedly in $GaAs_{1-x}P_x$ alloys, where it has also been studied in some detail[14–21] and found to exhibit a behavior very similar to the case of $Ga_{1-x}Al_xAs$ alloys: similar ionization energy (0.3–0.4 eV), an energy level located at about 170 meV from the *X* band, large distribution of

TABLE I. List of the various III-V alloys in which electrical measurements have been performed and given experimental evidence of *DX* centers in *n*-type-doped materials. The range of alloy composition *x* where the *DX* center is observed is reported in the fourth column. The nature of the associated donor impurity is indicated when known. The second and third columns illustrate the composition range in which the existence of the *DX* center (originating from the *L* or *X* valleys) is predicted, according to the proposed criterion. The fulfillment of this criterion for both the *L* and *X* valleys does not imply the existence of two deep levels: in this case, there still should be one deep state only, associated with either *L* or *X* or a mixture of *L* and *X* valleys, depending on their relative position.

		x value		
Alloys	Prediction *X*	Prediction *L*	Experimental observations	References
$Ga_{1-x}Al_xAs$	0.4–1	0.3–0.9	0.2–1 (Si, Se, Te, Sn)	9–11
$In_{1-x}Ga_xP$	0.7–1	0.6–0.9	0.5:No	unpublished
$In_{1-x}Al_xAs$	0.6–1	0.5–1	>0.5	24
$Ga_{1-x}Al_xSb$	0.3–1	0–0.9	$0>0.2$ (Te) 0 (S,Se,Te) >0.4 (Te)	22
$As_{1-x}P_xIn$			No	?
$In_{1-x}Ga_xSb$		0.9–1	0:No	25
$Sb_{1-x}As_xGa$	?	?	?	
$As_{1-x}P_xGa$	0.3–1	0.4–0.6	0.3–0.6 (S, Te)	12–19
$In_{1-x}Al_xP$	0.4–1	?	?	
$Ga_{1-x}In_xAs$			0.5:No	unpublished

electron capture rates, etc. In that case [see Fig. 1(a)], it appears that the *DX* center is associated with the *X* band,[15,21] we understand this because the *L*-associated state is higher in energy and thus remains a shallow excited state. The range in which we predict the *DX* center to exist is $0<x<0.7$.

3. $In_{1-x}Al_xP$, $As_{1-x}P_xIn$, and $Sb_{1-x}As_xGa$. In the $As_{1-x}P_xIn$ [Fig. 1(c)] alloy we predict the absence of a *DX* level localized in the gap. In $In_{1-x}Al_xP$ [Fig. 1(h)] the *DX* center, at least originating from the *X* band (the position of the *L* band is not known to our knowledge), should exist for $x>0.4$. Confirmation by experimental observations is not possible since, to our knowledge, there has not yet been any defect study in these materials. Concerning the $Sb_{1-x}As_xGa$ alloy, it is not possible to make any prediction since the band structure is not correctly known.

4. $GaAl_{1-x}Sb_x$. The existence of the *DX* center associated with S, Se, and Te doping in this alloy has also been established,[22–25] in particular, in GaSb.[23] As it is predicted, the character (*X* or *L*) of the *DX* level is observed to change in the $x=0.5-1$ range[24,25] since the *X*-associated state is deeper in energy than the *L*-associated state in this *x* range and higher in the complementary range [see Fig. 1(f)]. There is, therefore, a correct agreement between prediction and observation.

5. $InAl_{1-x}As_x$. We are only aware of one work[26] on donor-induced defects in this alloy. It confirms that a defect similar to the *DX* center appears for $x>0.5$. This is indeed in agreement with the prediction [Fig. 1(g)].

6. $InGa_{1-x}Sb_x$. For these alloys no data relative to donor-associated defect exist, except for InSb.[27] The *DX* state is then resonant in this conduction band, since it only emerges in the gap under hydrostatic pressure (700 MPa). This is what is predicted for $x=0$ [see Fig. 1(e)].

7. $InGa_{1-x}P_x$. In this case, data are available only for donor-associated defects in $In_xGa_{1-x}As_yP_{1-y}$ alloys,[28–30] the band structure of which is not known in the whole range of *x*,*y* compositions. Yet the data only correspond to specific couples of *x*,*y* values. Therefore, the range of composition predicted for the existence of the *DX* center cannot be checked. Nevertheless, *DX*

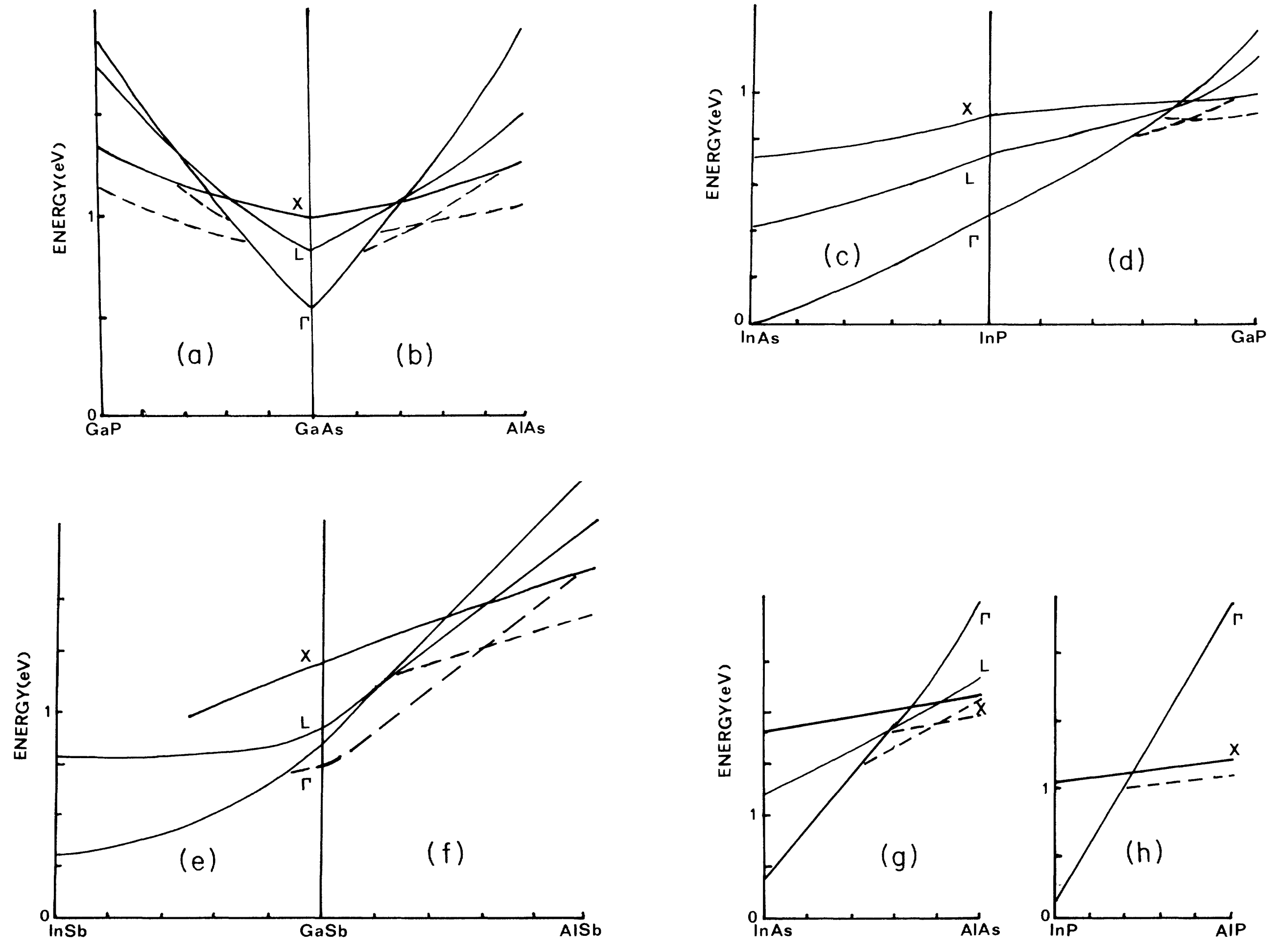

FIG. 1. Variation of the bottoms of the Γ, L, X conduction bands vs alloy composition for the following alloys: (a) $As_{1-x}P_xGa$, (b) $Ga_{1-x}Al_xAs$, (c) $As_{1-x}P_xIn$, (d) $In_{1-x}Ga_xP$, (e) $In_{1-x}Ga_xSb$, (f) $Ga_{1-x}Al_xSb$, (g) $In_{1-x}Al_xAs$, and (h) $In_{1-x}Al_xP$. The vertical energy scale is indicated by number in eV, and the predicted locations of the *X*- and *L*-associated *DX* levels are given by the dashed lines.

states are indeed observed in the range $0<y<0.4$ for x varying between 0.3 and 0.5. Our recent DLTS studies in $Ga_{1-x}In_xP$ confirm the prediction of the nonexistence of DX centers for an alloy composition $x \sim 0.50$ [Fig. 1(d)].

8. $GaIn_{1-x}As_x$. In this case, the DX center should not exist, because the X and L bands remain always more than 0.2 eV above the Γ band. We have verified this conclusion, through using capacitance spectroscopy (DLTS) experiments, for $x=0.5$.

III. INTERVALLEY MIXING MODEL

Table I demonstrates that there is a good correlation between our prediction and the experimental observations in all the cases where data are available. The existence of the DX level is thus closely related to the L or X valleys. The only feature which distinguishes these valleys from the Γ one is the fact that there is only one single Γ valley against $N=4,3$ valleys for L and X, respectively. Hence the idea that intervalley mixing plays a key role in the formation of a deep DX level.[6,31,32]

In the presence of intervalley mixing, the potential to be used in the EMA Schrödinger equation of the envelope wave function associated with the donor is the potential $V(r)$ modulated by a spatial renormalization factor $|\Phi(0,\mathbf{r})|^2$.[33,34] The standing wave function with the appropriate symmetry of the ground state is a linear combination of the unperturbed crystal Bloch states $\psi_c^0(k_\mu,\mathbf{r})$ corresponding to the conduction band around the N equivalent minima k_μ. At this stage of the analysis, it is postulated that the ground state has the A_1 symmetry, in which case

$$\Phi(0,\mathbf{r})=\sum_{k=0}^{7}\frac{1}{\sqrt{N}}\psi_c^0(\mathbf{k}_\mu,\mathbf{r}) . \tag{1}$$

Within a few percent, $\psi_c^0 \sim 1$ at $r=0$, which leads to fully constructive interference effects near the origin. The phase coherence is lost at a typical distance r_0 such that $|k_\mu|r_0|\sim 1$, so that we can make the approximation

$$|\Phi(0,\mathbf{r})|^2=\begin{cases} N & \text{for } r<r_0 \\ 1 & \text{for } r>r_0 . \end{cases} \tag{2}$$

The basic idea is that the enhancement of the attractive potential $V(r)$ in the core region $r<r_0$ by a factor N is responsible for the deep nature of the DX ground state. This factor N is clearly due to the A_1 symmetry of the ground state, Eq. (1) being then a simple superposition of the μ components. As a matter of fact, in the intervalley EMA equation, only A_1 levels which have nonzero wave functions at the origin can go deep. We have already pointed out[6] that our interpretation of the DX level in terms of the intervalley EMA is thus in contradiction with a prior work of Morgan.[35] Using qualitative tight-binding arguments, this author proposed that the DX level originates from a T_2 state and not an A_1 state, as a result of a huge Jahn-Teller distortion. However, it is now understood from more recent tight-binding calculations[36] that the DX level originates from the A_1 state, and not from the T_2 states, which justifies our approach.

Note that we used the intervalley EMA to explain the existence of a deep state related to the L or X valleys; let us show now that this deep state is unique, i.e., all the other states are necessarily shallow. To fix the ideas, let us assume that the DX level is related to the L valleys (the demonstration is the same in case it is bound to the X valleys). A very simple demonstration can be made using the Green-function formalism to solve the intervalley EMA. Since r_0 is the order of the lattice parameter in Eq. (2), the factor $|\Phi(0,\mathbf{r})|^2$ leads to an additional central-cell correction. Let us call δV this central-cell correction. Let G_0 be the Green function of the EMA equation with the effective potential replaced by the Coulomb potential alone, and G be the Green function of the EMA equation including the term δV (which is allowed to be large). Assuming that G_0 is known, G is given by the Dyson's equation

$$G-G_0=\delta G=G_0\delta V G . \tag{3}$$

The problem is then readily solved following the Koster-Slater impurity model.[37] Equation (3) can be solved by iteration:

$$\delta G=G_0(\delta V+\delta V G_0 \delta V+\cdots)G_0 . \tag{4}$$

Since δV is a central-cell correction, the Dyson's equation is most easily solved if we express it in the Wannier representation. Let $\langle m\rangle$ denote the Wannier state at site m, and $\langle 0\rangle$ designate the donor site. The only nonvanishing matrix element of δV is $U=\langle 0|\delta V|0\rangle$. Then, by injecting the closure relation $\sum_p |p\rangle\langle p|=1$ between the operators in Eq. (4), Eq. (3) can be cast under the form

$$\begin{aligned}\langle n|\delta G|m\rangle &=\langle n|G_0|0\rangle(1+U\langle 0|G_0|0\rangle+\cdots) \\ &\quad\times U\langle 0|G_0|m\rangle ,\end{aligned} \tag{5}$$

that is,

$$\langle n|\delta G|m\rangle=\frac{\langle n|G_0|0\rangle U\langle 0|G_0|m\rangle}{1-U\langle 0|G_0|0\rangle} . \tag{6}$$

The poles of the Green function in the presence of the central-cell correction are thus located at the energy solutions of the equation

$$-U\,\mathrm{Re}\langle 0|G_0|0\rangle=0 . \tag{7}$$

(Re means the real part.) Let ψ_n designate the eigenfunction of the Hamiltonian without the central-cell correction, for the eigenenergy E_n. Then ψ_n is also the basis which diagonalizes G_0. The use of the closure relation implies that Eq. (7) can be written

$$\langle 0|G_0|0\rangle=|\langle 0|\psi_n\rangle|^2\langle\psi_n|G_0|\psi_n\rangle \tag{8}$$

so Eq. (7) becomes

$$F(E)=\sum_n\frac{|\langle 0|\psi_n\rangle|^2}{E-E_n}=\frac{1}{U} . \tag{9}$$

In the energy gap, the E_n spectrum is discrete and reduces to the Palmer series of the shallow hydrogenic levels relative to an electron with effective mass m^* in an effective medium of dielectric constant ε. The variation of $F(E)$ as a function of E is illustrated in Fig. 2. The solutions of Eq. (9) are given by the intercept of the curve $F(E)$ with the straight line parallel to the x abscissa at the ordinate $1/U$. Of course, if the potential U is positive, all the energy solutions of Eq. (9) are higher than the 1*s* hydrogenic level E_1 so that all the levels are shallow. For an attractive central-cell correction (U large and negative), we can see that the ground level goes deep below E_1. However, all the other levels are shallow at an energy strictly larger than E_1.

At this stage we have shown that only one deep state can be related to one type of valley (say the L valleys), but the existence of the X valleys has been neglected. We can argue that these x valleys cannot generate a second deep level either, by using the pseudopotential concept: let ψ be the ground state related to the L valleys, with the energy ε_1, so that, if H is the Hamiltonian,

$$H|\Psi\rangle=\varepsilon_1|\Psi\rangle \ . \tag{10}$$

Any excited state with a dominant X character must be orthogonal to this ground state, so that it takes the form

$$\Psi_{\mathrm{ex}}=\Phi-\langle\Psi|\Phi\rangle\Psi \ . \tag{11}$$

The substitution of Eq. (11) into the Schrödinger equation

$$H\Psi_{\mathrm{ex}}=E_{\mathrm{ex}}\Psi_{\mathrm{ex}} \tag{12}$$

taking Eq. (10) into account, leads to

$$H|\Phi\rangle+\langle\Psi|\Phi\rangle(E_{\mathrm{ex}}-\varepsilon_1)|\Psi\rangle=E_{\mathrm{ex}}|\Phi\rangle \tag{13}$$

which can be written under the form of a Schrödinger equation on $|\Phi\rangle$, of the kind

$$(H+V_p)|\Phi\rangle=E_{\mathrm{ex}}|\Phi\rangle \ . \tag{14}$$

V_p is an additional central-cell correction such that

$$V_p|\Phi\rangle=(E_{\mathrm{ex}}-\varepsilon_1)\langle\Psi|\Phi\rangle\Psi \ . \tag{15}$$

Note that $E_{\mathrm{ex}}-\varepsilon_1$ is positive, since E_{ex} is the energy of an excited state, so V_p is a repulsive central-cell contribution, which prevents the excited level to be deep. This is in essence why, in general, there can be only one deep state associated to the *DX* center.

The description of this deep state is at the limit of validity of the EMA. A deep state is normally a combination of all conduction-band states.[4] However, it is possible to treat each subband separately, in a variational manner, and, if one of them (that of the L states in the occurrence) leads to a much more stable state than the others,[6] then it dominates the situation. Indeed, tight-binding calculations[4] give evidence that the *DX* ground state retains a dominant L character. This is due to the prominent peak of the L states which dominates the density of states of the conduction band. A confirmation that L and not X drives the *DX* center deep in this alloy is the observation of an almost site independence of the *DX* binding energy. We have already mentioned earlier in this work that only A_1 levels, which have nonzero wave functions at the origin can become deep as a result of the central-cell correction, and at X, they must come from X_1 bands (yielding A_1+E), not X_3 (yielding T_2 only). Substituting the anion X_1 is the lowest band, whereas substituting the cation X_1 is higher than X_3, by as much as 0.5 eV in pure AlAs. Then, a Si dopant (on an As site) should produce a considerably less bound *DX* center than a Se dopant (on a Ga site), for example, contrary to the experimental result. On the other hand, the L_1 band is always the lowest for both anion and cation substitutionals, yielding A_1+T_2, hence a deep almost site independent A_1.

Therefore, we believe that the EMA is a reasonable approximation to describe the electronic states of the *DX* centers on a qualitative basis. Yet, the solution of the EMA effective Hamiltonian requires the choice of the effective potential $V(r)$, and, as we shall see in Sec. IV, this is a major problem.

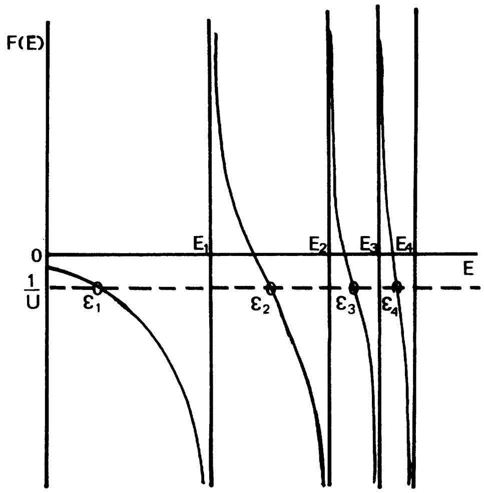

FIG. 2. Poles of the Green function in the presence of a central-cell potential showing that only the ground-state energy ε_1 can be deep, those of the excited states $\varepsilon_i (i>1)$ remaining the order of the energies E_i of the shallow EMA states without central-cell correction.

IV. THE CAVITY MODEL: $V(r)=-e^2/\varepsilon(r)r$

The cavity model has been used for decades to explain the shallow-deep instability of donors in semiconductors.[6,38–42] The basic idea is that the Coulomb potential experienced by the donor electron is $e^2/(\varepsilon r)$ in conventional notations, for $r>r_0$, where r_0 is the order of the size of the Wigner-Seitz cell. For $r<r_0$, however, the bare Coulomb potential remains unscreened, so we can write (see Ref. 6, and references therein)

$$V(r)=-\frac{e^2}{\varepsilon_0 r}+\frac{e^2}{\varepsilon_0 r_0}\left[1-\frac{\varepsilon_0}{\varepsilon}\right] \ , \quad r<r_0 \tag{16a}$$

$$V(r)=-\frac{e^2}{\varepsilon r} \ , \quad r>r_0$$

which can be cast under the form $V(r)=e^2/[r\varepsilon(r)]$, with a spatial-dependent dielectric function. Thus, one has to solve the Schrödinger equation for an electron in a potential $|\Phi(0,r)|^2V(r)$, with the following spatial dependence of the electron mass:[39,42]

$$m(r)=m_0 \text{ for } r<r_0 \text{ and } m^* \text{ for } r>r_0 \ . \tag{16b}$$

The spatial dependence of $\varepsilon(r)$ and $m(r)$ are corrections to the effective-mass approximation which, otherwise, would break down in the central-cell region $r<r_0$. The solution of the Schrödinger equation can be written[42]

$$\psi_{vlm}=M_{vlm}R_{vl}(r)Y_{lm}(\theta\varphi) \tag{17}$$

where M is a normalization coefficient, Y_{lm} the spherical harmonics, and R_{vl} the radial functions

$$\begin{aligned} R_<(r)&=A_{uvl}(\rho^*)^l\exp(-\rho^*/2)\ , \quad r<r_0 \\ R_>(r)&=B_{vl}\rho^l\exp(-\rho/2)\ , \quad r>r_0 \end{aligned} \tag{18}$$

where the reduced variables are

$$\rho^*=\frac{2N}{\nu^*}\frac{r}{a_b}\ , \quad \rho=\frac{2}{\nu}\frac{\varepsilon_0}{\varepsilon}\frac{m^*}{m_0}\frac{r}{a_B}\ , \tag{19}$$

where a_B is the atomic Bohr radius; u and v are the solutions of a confluent hypergeometric equation. We require that $R(r)$ is regular at $r=0$ and $r\rightarrow\infty$, which implies

$$\begin{aligned} u&=A\phi(l+1-\nu^*\ ,2l+2,\rho^*)\ , \quad r<r_0 \\ \nu&=B\Psi(l+1-\nu\ ,2l+2,\rho)\ , \quad r>r_0 \end{aligned} \tag{20}$$

where θ and Φ are the Tricomi function and the Kummer's series, respectively. The boundary conditions are[6]

$$\begin{gathered} R_<(r_0)=R_>(r_0)\ , \\ \frac{1}{m_0}\frac{dR_<(r_0)}{dr}=\frac{1}{m^*}\frac{dR_>(r_0)}{dr}\ . \end{gathered} \tag{21}$$

The ground state is an s state, so that we set $l=0$ in the equations, in which case it is a simple matter of algebra to reduce Eq. (21) under the form[6]

$$-(1-\nu^*)\frac{\phi(2-\nu^*,3,\rho_0)}{\phi(1-\nu^*,2,\rho_0)}+\frac{\nu^*}{\nu N}\frac{\varepsilon_0}{\varepsilon} \times\left[1-\frac{2}{\rho_0}\frac{\Psi(-1-\nu,-1,\rho_0)}{\Psi(-\nu,0,\rho_0)}\right]=0\ , \tag{22}$$

where ρ_0,ρ_0^* are the values of ρ and ρ^* for $r=r_0$. The principal quantum numbers ν and ν^* are related to the energy E of the donor levels according to the relations

$$\begin{gathered} \nu^2=-\frac{m^*e^4}{2\varepsilon^2h^{-2}E}\ , \\ \frac{1}{2(\mu^*)^2}=\frac{1}{N^2}\frac{m^*}{m_0}\left[\frac{\varepsilon_0}{\varepsilon}\right]^2\frac{1}{2\nu^2}+\frac{1}{N}\frac{a_B}{r_0}\left[1-\frac{\varepsilon_0}{\varepsilon}\right]\ . \end{gathered} \tag{23}$$

Note in general ν and ν^* are not integers here.[6,42]

The numerical calculations then require a value for ε and m^*($\varepsilon\simeq 13$ in $\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{As}$). In a prior work[6] the equations have been solved; for the choice $m^*=0.56m_0$ for L valleys. The solution has been illustrated under the form of the variations of the quantum number ν and the binding energy $-E$ as a function of the cutoff parameter r_0 in the vicinity of the shallow-deep instability. Similar plots have been also reported by Chandhuri and Coon with application to interstitial impurities in semiconductors; for example, see Ref. 42.

There is, however, a hidden artifact in this procedure: the plots recorded so far in the literature for ν and E are *not* related to the ground state. The reason is that the radius of the Wigner-Seitz cell of the lattice r_0 is much larger than a_B($\simeq 0.5$ Å). As a consequence the ground state is essentially a 1s atomic hydrogenic state; since the extension of its wave function is a_B, an electron in this ground state experiences only the region $r\leq r_0$ where the base Coulomb potential is unscreened, so its eigenenergy is about 1 Ry. Therefore, the ground state of the Schrödinger equation, with $V(r)$ given in Eq. (16), is always a 1s-hydrogenic state located about 13 eV below the bottom of the conduction band. This has presumably not been realized before since a lot of effort has been devoted to a more accurate description of the screening of the electrostatic charge (see, for example, Refs. 33, 34, 41, 43, and 44). In all cases, the refinements amount to replacing Eq. (16) by $V(r)=e^2/[\varepsilon(r)r]$, with a continuous r-dependent dielectric constant, and various models of $\varepsilon(r)$. However, in all semiconductors, the electrostatic charges are screened near the impurity site. Therefore, all the models of dielectric constants have in common the fact that $\varepsilon\sim 1$ for $r\leq a_B$, and as we have shown earlier, this is sufficient to push the $A_1(1s)$ level off the conduction band. Therefore, such refinements are useless. An additional proof can be found in Ref. 33, where the authors reported that the numerical value of the binding energy of the $A_1(1s)$ ground state is several times the fundamental gap when it is computed from the EMA equation, with m^*, $\Phi(0,\mathbf{r})$ and $\varepsilon(r)$ relevant to silicon, $\varepsilon(r)$ being derived in a Thomas-Fermi screening model. For the same reason, refinements on $\Phi(0,\mathbf{r})$ (Refs. 33 and 34) will not modify this result either.

Within the cavity model, it is thus the first excited $A_1(2s)$ level which is a good candidate for the shallow-deep instability, not the ground level which is *always* deep, for *any* donor impurity. This is best evidenced in Fig. 3 which illustrates the wave function of the A_1 donor state associated to the L valleys in Ref. 6, for the value $r_0=1.7$ a.u. yielding a binding energy 0.2 eV. The wave function presents a node and is then clearly a 2s orbital. The same result has been reported in Ref. 33, for the particular case of the EMA applied to silicon. This feature has been missed in the other works.[6,38–45] The reason is that attention has been focused on the principal quantum number ν. However, ν has a physical meaning for the region $r>r_0$ only. Since the wave function is mainly localized in the region $r\leq r_0$, the relevant quantum number is ν^* and not ν. We indeed find $\nu^*=2.0$ within an accuracy 10^{-3} for the state in Fig. 3.

These results force us to reconsider the relevance of the cavity model. It is usually believed that the cavity model

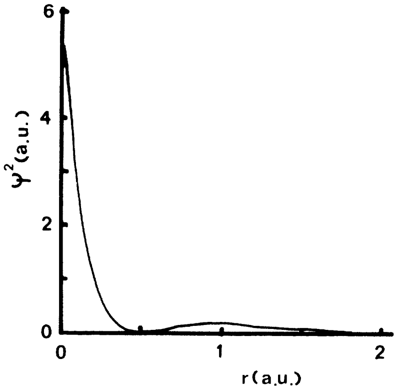

FIG. 3. Spatial extension (ψ^2 vs r, in a.u.) of the wave function for the A_1 donor state, located at 200 meV below the L band, calculated in the model of Ref. 6.

applies to donor impurities, whenever their ground energy level is deep into the gap.[33,34,38–45] For example, it is taken for granted that the cavity model, i.e., the impurity potential $V(r)=-e^2/\varepsilon(r)r$ is appropriate for interstitial donor impurities in silicon such as hydrogen and lithium impurities.[33,46] To the contrary, we claim that this kind of impurity potential is *never* justified because the fact that the $A_1(1s)$ level is deep is actually an artifact due to the screening effect of the electrostatic charges implying $\varepsilon(r)\sim 1$ for $r<a_B$. The proof is that, in this model, all the donors in all the semiconductors should have a deep ground level. Incidentally, the binding energy should not exceed the energy gap. The 1-Ry binding energy in the model is thus unphysical and due to the fact that the coupling of the impurity donor states with the valence-band states must be taken into account when the binding energy is not small with respect to the gap. Moreover, the common procedure which amounts to forgetting the existence of this deep $A_1(1s)$ state and discussing the shallow-deep instability, or even fitting the experimental value of the binding energies as if the $A_1(2s)$ state was the gap. Moreover, the common procedure which amounts to forgetting the existence of this deep $A_1(1s)$ state and discussing the shallow-deep instability, or even fitting the experimental value of the binding energies as if the $A_1(2s)$ state was the real ground state in the framework of the cavity model, is meaningless: we have argued in the preceding section that an impurity should not have more than one deep bound state in a semiconductor. Therefore, the fact that the $A_1(2s)$ level can go deep is just another artifact of the model. The fundamental reason here does not come from the particular choice of the impurity potential, but rather from the EMA itself. In effect, the EMA reduces the Schrödinger equation to that of a free electron in a local potential. This Hamiltonian thus admits an unbound continuum of eigenstates, in violation with the Bloch theorem which implies that the bands have a finite width due to the periodic crystal field. The EMA is thus valid only when the impurity potential is small as compared with the bandwidth of the conduction band. This condition is violated for impurity potentials leading to a shallow-deep instability for the $A_1(2s)$ state. We believe this is the key problem with the impurity potential $-e^2/[\varepsilon(r)r]$ which is not only large for $r<r_0$, but even diverges at $r=0$. In EMA, one wants to write the impurity wave function in terms of the states of the lowest conduction bands. Then one has to calculate the potential matrix elements in this finite basis set. If one wants to have a picture of these elements in real space, one has then to transform this matrix to the real-space basis formed by the Wannier functions. In this picture, the diagonal elements $\langle W_{n,0}|V|W_{n,0}\rangle$ of the Wannier functions at the impurity site $\mathbf{R}_0$ do not diverge, while more distant ones obviously behave as $\langle W_{n,0}|V|W_{n,\mathbf{R}}\rangle=-e^2/[\varepsilon R]$. It follows that the relevant potential $V(r)$ entering the EMA equation is regular at $r=0$ like the pseudopotential used by Resca and Graft[47] for Si impurities in silicon.

V. AN EMA MODEL FOR THE SHALLOW-DEEP INSTABILITY WITH APPLICATION TO THE *DX* CENTER IN $\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{As}$

Although the procedure to build realistic pseudopotentials is known,[48] the expression of $V(r)$ for the *DX* center in III-V compounds is unknown. A semiempirical approach consists in keeping the expression of $V(r)$ as given in Eq. (16) for $r>r_0$ since it is the correct asymptotic form for large r, and take $V(r)$ constant at $r\le r_0$ to remove the divergence of the Coulomb potential:

$$\begin{aligned} V(r)&=-\frac{e^2}{\varepsilon r}\ , \quad r>r_0 \\ V(r)&=V_0\ , \quad r<r_0\ . \end{aligned} \tag{24}$$

Note in the case of substitutional impurities, V_0 also includes the central-cell correction associated to the substitution of the host element by a different chemical species. It is then convenient to rewrite this potential as

$$V(r)=V_1(r)+V_c(\mathbf{r})\ , \tag{25}$$

where

$$\begin{aligned} V_1(r)&=-\frac{e^2}{\varepsilon r}(r\ge r_0)\ , \\ V_1(r)&=-\frac{e^2}{\varepsilon r_0}(r\le r_0)\ . \end{aligned} \tag{26}$$

Then

$$V_c(r)=V(r)-V_1(r) \tag{27}$$

represents the central-cell correction since it differs from zero only for $r\le r_0$, in which region it is a constant. Note that the potential $V(r)$ thus defined is discontinuous (except if $V_c=0$). In principle, one might object that the derivation of the EMA equation requires that $V(r)$ varies smoothly at the scale of the lattice parameter. Nevertheless, the patent success of the EMA in the derivation of the eigenstates and dispersion relations of minibands of superlattices, where the potential varies discontinuously at the interfaces between adjacent layers, proves that a discontinuity of $V(r)$ does not affect the validity of the EMA. The objection that a discontinuity of the pseudopotential $V(r)$ is unphysical is not serious either, because we do not pretend to achieve a quantitative description of the *DX* center, far beyond the EMA: we only aim to get some insight on the physical origin of the electronic properties, which do not depend on such details as whether the pseudopotential varies sharply or discontinuously in the vicinity of the central cell. In particular the pseudopotential used here inside the central cell is not the one, composed of an attractive Coulomb part and of a core repulsive part, considered in tight-binding calculations. Instead, our choice of the pseudopotential averages the true potential over the elementary cell. This choice is actually implied by the fact that it is crucial, within the EMA, to deal with a potential which is small everywhere. A potential, which shows important peaks inside the unit cell as a result of the repulsive core potential and Coulomb potential, does not satisfy this criterion and is not compatible with the use of the EMA when the electron density is large in this region. This average value of the pseudopotential inside the central cell is determined by the condition that it reproduces the binding energy of the Γ effective-mass state.

The EMA equation to be solved for the envelope function $F(\mathbf{r})$ is now

$$-\frac{\hbar^{2}}{2}\nabla\left[\frac{1}{m(\mathbf{r})}\nabla\psi(r)\right]+V(\mathbf{r})|\Phi(0,\mathbf{r})|^{2}\psi(r)=E\psi(\mathbf{r}) \tag{28}$$

with $m(\mathbf{r})$, $V(\mathbf{r})$, and $\Phi(0,\mathbf{r})$ given in Eqs. (16) and (1), respectively. The solution for the radial part of the envelope function is

$$\begin{aligned} R_{<}(r)&=A\left[\frac{k}{r}\right]^{1/2}J_{I+1/2}(k,r)\;, \quad r<r_0 \\ R_{>}(r)&=B\Psi(I+1-\nu\;,2|+2,\rho)\rho^{I}e^{-\rho/2}\;, \quad r>r_0 \end{aligned} \tag{29}$$

with

$$k=\frac{1}{\hbar}[2m(-NV_0-|E|)]^{1/2}\;. \tag{30}$$

$R_{>}(r)$ has the same expression as in the cavity model; its expression has been recalled for completeness. $J_{I+1/2}$ is the Bessel function of index $I+1/2$. After some calculations reported in Appendix A, we find that the boundary conditions [Eq. (24)] lead to the following equation for the energy E of the ground state:

$$\frac{2}{\rho_0}\left\{-2(1+\nu)\frac{I(-1-\nu,-1;\rho_0)}{I(-\nu,0;\rho_0)}+\frac{m^*}{m_0}[1-kr_0\mathrm{cotg}(kr_0)]\right\}+1=0\;, \tag{31}$$

where I is the following integral:

$$I(a,c;\rho)=\int_0^{\pi/2}(\cos x)^{-c}\cos\left[\frac{\rho}{2}tgx+(2a-c)x\right]dx\;. \tag{32}$$

Since ν depends on the energy E [see Eq. (23)], Eq. (31) is an equation for E, which can be solved numerically.

We have applied this model to $Ga_{1-x}Al_xAs$, since it is the material where the *DX* center has been most investigated. The *DX* ground level is mainly bound to the L valleys in this case. These valleys are very anisotropic, with $m_T<m_L$, where m_T,m_L are the transverse and longitudinal masses, respectively. Since the anisotropy is ignored in our model, one can wonder which value of m^* is relevant to this case. Faulkner has solved the classical EMA equation, taking the anisotropy into account.[49] The result of the exact calculation is that the energy of the 1*s* state is close to the value it should have for the isotropic case with $m^*\sim m_T$. In particular, the choice of the effective mass of the density of states for m^* widely underestimates the binding energy. That is why in the present case, we choose $m^*=m_T=0.08m_0$ and we set r_0 equal to the radius of the Wigner-Seitz cell, namely $r_0=5.5$ a.u. Under such conditions, the 1*s* ground level of Eq. (31) in the absence of the central-cell correction V_c is shallow. A deep level at an energy $E=-0.2$ eV is obtained only for $V_c(r<r_0)=0.627$ eV. Note that this value is quite reasonable since a central-cell correction for the pseudopotential associated to a substitutional donor is expected to be a fraction of an electron volt. For a single valley, like an extremum at the Γ point, such a potential only shifts the ground state by a few meV. For the L multivalley case, however, the enhancement by a factor $N=4$ in the core region [see Eq. (2)] forces the ground state to be on the deep side of the shallow-deep instability. This is illustrated in Fig. 4 where we have reported the variation of the binding energy as a function of $V_c(r<r_0)$ for the parameters $m^*=0.08m_0$, $\varepsilon=13$, $N=4$ appropriate to $Ga_{1-x}Al_xAs$. The shallow-deep instability occurs for $V_c(r<r_0)=0.53$ eV. This means that the X-associated state ($N=3$) remains below the instability, i.e., shallow. This calculation illustrates that the role of the central-cell correction has been grossly underes-

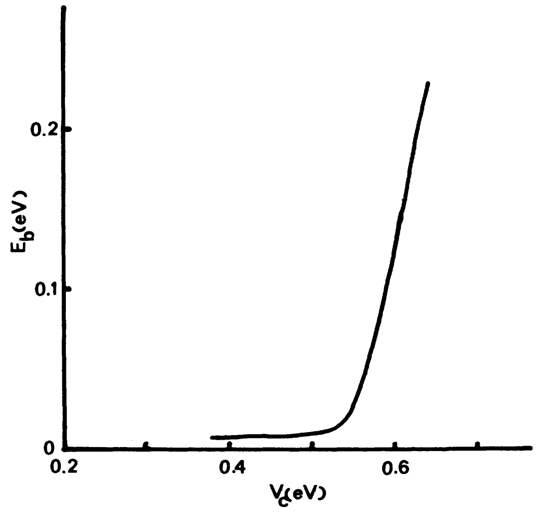

FIG. 4. Variation of the binding energy E_b calculated as a function of the depth of the central-cell potential V_c.

timated in our prior work[6] and more generally in all the models of deep levels based on the cavity model. Our result is in agreement with the result of Green-function studies of impurity levels in multivalley semiconductors[50] according to which an impurity level goes deep under the combined effect of a high projected density of states and a sufficiently strong central-cell correction.

Figure 5 also illustrates that the binding energy of the intervalley effective-mass equation is sensitive to the central-cell contribution of specific impurity pseudopotentials in the shallow-deep instability region. This, of course, represents an overestimate, since the interaction with valence states becomes increasingly important as the impurity level is deeper, hence a repulsion from valence states, not taken into account in the model. Nevertheless, such a repulsion from the valence band should not smear out the dependence of the binding energy upon $V_c(r<r_0)$. This dependence may be at the origin of the qualitative difference in the electronic structure of various impurities in semiconductors. For instance, according to Figs. 10 and 12 of Ref. 51, Sb, S, and Se in AlAs have binding energies of about 0.2 eV while Te is shallow, but that of Si is about 0.6 eV. Also in Si, it has been argued that group-V substitutional donors produce central-cell pseudopotentials weak enough to keep them at the shallow edge of the instability.[50] The same may hold true in Ge.

Another feature of our model is that the binding energy ($\sim$0.2 eV) of the *DX* center is smaller than the Coulomb energy at the edge of the central cell $e^2/(\varepsilon r_0)$, as it is illustrated in Fig. 5. This is a clear evidence that the Coulomb tail plays a much more significant role than acknowledged before. This important feature accounts for the fact that the electron emission of the *DX* center is sensitive to an applied electric field through a so-called Poole Frenkel effect,[52] a property which could not be understood in the absence of a long-range potential. Indeed such a sensitivity on the electric field cannot be observed for deep defects.

We also note that the wave function of the *DX* electron in its ground state is strongly localized, as it can be seen in Fig. 6. Such a strong localization means a high-electron density close to the impurity site, which favors a strong electron-lattice interaction. Starting with the model of Toyozawa,[53] with the trial electron wave function

$$\psi(r)=\frac{1}{\sqrt{\pi a^3}}e^{-r/a} \tag{33}$$

one finds that the kinetic term scales like a^{-2}, the Coulomb energy scales like a^{-1}, and both the short-range contribution of the central-cell correction U_{SR} and the electron-lattice coupling term corresponding to a position-dependent dilatation scale like a^{-3}. With this regard, the electron-lattice interaction may well be included in our model, and only amounts to a renormalization of the central-cell potential. It is then possible that a fraction of the central-cell potential comes from the electron-phonon interaction, the remaining part originating from the chemical difference between the impurity and the host element to which it is substituted.

In this spirit, the electron-phonon interaction induces a local lattice relaxation but a negligible (if any) static Jahn-Teller distortion. Indeed the barrier for electron capture is equal (within the experimental accuracy) to the energy difference between the L band and the bottom of the conduction band,[54] except in the case of Si where a 200-meV constant must be added to this energy.[11] This can only be understood if electron capture occurs through a cascade mechanism via the excited state associated with the L band. This capture cannot take place via the excited states of the bottom of the conduction band since the corresponding excited states cannot be filled at the temperature the process occurs.[55]

Finally, the potential $V(r)$ illustrated in Fig. 5 only represents an average of the pseudopotential over the angular spherical coordinates. It then does not allow any investigation of the shallow excited states. The reason is

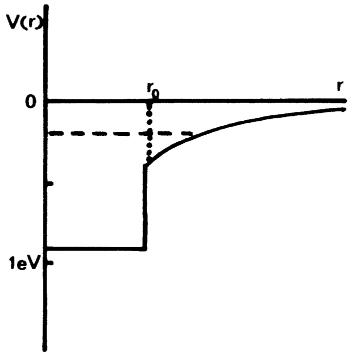

FIG. 5. Pseudopotential of a donor impurity in $\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{As}$ giving rise to a binding energy of the ground state equal to 200 meV for the case of L valleys, illustrated by the horizontal broken curve ($r_0=5.5$ a.u., $m^*=0.08m_0$, $\varepsilon=13$). The binding energy of the ground state for this potential is only a few meV in case of a Γ valley.

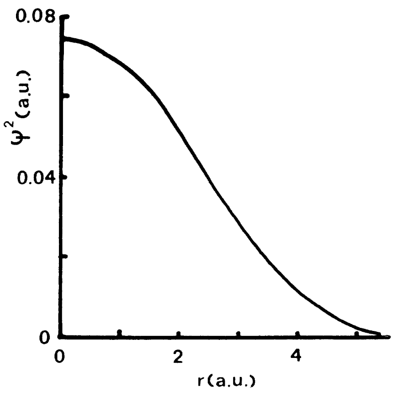

FIG. 6. Spatial extension (ψ^2 vs r, in atomic units) of the calculated ground-state wave function of the L associated state for a binding energy of 200 meV, according to the model of the present work.

that such states are very sensitive to the anisotropy, which, for example, splits the p states into p^0, and $p^{+,-}$ states. For the large anisotropy observed in III-V compounds, the energy splitting is so large that the first excited states are the $2p^0$ states instead of the $2s$ state.[49] The spherical approximation is thus relevant only to the study of A_1 states, including the ground state.

VI. CONCLUSION

After a careful reconsideration of the treatment of the cavity model in the case of intervalley mixing, we have shown that the donor impurity in III-V alloys, if accompanied by a central-cell correction of normal magnitude (~ 0.6 eV) has a deep ground state (0.2 eV below the L valleys in the archetype alloys $\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{As}$), while all the excited states remain shallow. Although the corresponding wave function of the ground state is rather localized, it remains nonetheless sensitive to the Coulomb tail of the binding potential. This result justifies the existence of a *DX* center made of a substitutional impurity, the electron-phonon interaction inducing only a lattice relaxation but no distortion. Such a model is verified by the correlation between the observation of the *DX* center in various III-V alloys and the nature of their band structure.

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APPENDIX A

The equation for the energy in our model is provided by the boundary condition [Eq. (21)], under the form

$$\frac{1}{m^*}\frac{d\ln R_>}{dr}=\frac{1}{m_0}\frac{d\ln R_<}{dr} . \tag{A1}$$

The logarithm derivative of J and Ψ functions can be determined from the recursion relations:

$$\begin{aligned}&\frac{d\ln[J_{l+1/2}(kr)]}{dr}=\frac{l+1/2}{r}-k\frac{J_{l+3/2}(kr)}{J_{l+1/2}(kr)} ,\\ &\frac{d\ln[\Psi(a,c;\rho)]}{d\rho}=1-\frac{\Psi(a,c+1;\rho)}{\Psi(a,c;\rho)} .\end{aligned} \tag{A2}$$

Making use of the relation

$$\Psi(a,c;\rho)=\rho^{1-c}\Psi(a-c+1,2-c+1;\rho) \tag{A3}$$

Eq. (A2) can be written under the form

$$\frac{d\ln[\Psi(a,c;\rho)]}{d\rho}=1-\frac{1}{\rho}\frac{\Psi(a-c,2-c+1;\rho)}{\Psi(a-c+1,2-c;\rho)} . \tag{A4}$$

The Tricomi and Bessel functions are easily evaluated from their representations:

$$J_{l+1/2}(kr)=(-1)^l(\pi kr/2)^{-1/2}(kr)^{l+1}\times\left\{\frac{d}{kr\,d(kr)}\right\}^l\left\{\frac{\sin(kr)}{kr}\right\} \tag{A5}$$

and

$$\Psi(a',c';\rho)=\frac{1}{\pi}2^{1-c}\Gamma(1-a')e^{\rho/2}I(a',c';\rho) \tag{A6}$$

valid for $\rho>0$, $\mathrm{Re}c'<1$. I is the integral defined in Eq. (32). Note that from Eq. (29), we have

$$a=I+1-\nu\ ;c=2l+2\ ; \tag{A7}$$

so that $c>1$. The use of Eq. (A3) to transform Eq. (A2) into Eq. (A4) is aimed at writing $d\ln R_>/dr$ as a function of Tricomi functions $\Psi(a',c';\rho)$ with real arguments $c'<1$, for which the integral representation (A6) holds. It is then straightforward to write Eq. (A1) under the form of Eq. (31) for the ground state, taking into account that this state has an A_1 symmetry, for which $l=0$.

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