

## Germanium negative- $U$ center in GaAs

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The  $DX$  center related to the Ge impurity in GaAs is investigated by *ab initio* pseudopotential calculations within the local-density approximation. Our results indicate that the behavior of the  $Ge_{Ga}$  defect is qualitatively different from the broken-bond model usually associated to  $Si_{Ga}$ , even if the electronic structure behaves in a very similar way. Indeed, for the Ge impurity our calculations show that already for breathing-mode relaxations of the Ge neighbors, in  $T_d$  symmetry, a negative- $U$  behavior is found, and many details of the experimental data can be explained.

### I. INTRODUCTION

A large body of experimental data concerning the so-called  $DX$  centers was collected in these past ten years.<sup>1</sup> The prototype center is the Ga-substitutional Si impurity in GaAs — which is also a prototype effective-mass donor impurity. In fact, Si doping of bulk GaAs, at zero pressure, efficiently produces  $n$ -type material, evidencing the preference for the Ga site in the lattice. At high pressures, however (higher than 22 kbar), or past a certain proportion  $x$  of Al in the alloy for  $Al_xGa_{1-x}As$  ( $x \geq 0.23$ ), a deep level is introduced in the gap, causing a dramatic drop in carrier concentration. It was recognized that this deep level originated from the isolated  $Si_{Ga}$  impurity, and theory pointed to a possible explanation in which a strong lattice distortion changed effectively the “shallow donor”  $d^0$  configuration to the deep trap  $DX^-$  configuration in the negative charge state.<sup>2,3</sup> It is to be expected that isoelectronic impurities like Ge and Sn behave similarly,<sup>1,4,5</sup> although less experimental work exists for these centers.

We present here a theoretical study of the Ga-substitutional Ge impurity in GaAs. We find that we can understand all the known data about the  $Ge_{Ga}$  center in light of our results, which indicate that the behavior of the  $Ge_{Ga}$  impurity is qualitatively different from that proposed for  $Si_{Ga}$ , even if the electronic structure behaves in a very similar way. We adopt the usual approach: supercell model, local-density approximation, with nonlocal core pseudopotentials. We include in the next sections a brief review of relevant results for  $DX$  centers, mostly for the sake of comparison between the Si and Ge impurities.<sup>2,3,6-8</sup> Details of our calculations and the discussion of our results follow, in Secs. IV and V.

### II. FINGERPRINTS OF $DX$ CENTERS: Si AND Ge

The forming of  $DX$  centers is mainly associated with the trapping of electrons, which results in a marked decrease in conductivity, and with the phenomenon of per-

sistent photoconductivity (PPC). In this latter case, the  $DX$  center is photoexcited, releasing the (trapped) electrons back to the conduction band; when the light is turned off, however, at low temperatures, the centers do not recapture electrons, so that the original resistivity is not restored. The recapture process is thermally activated, implying the presence of a barrier between the donor and acceptor configurations of the defect.

Both Si and Ge substituting for Ga form shallow donors in GaAs at zero pressure, and at a critical value of pressure  $p$  or Al concentration  $x$  in the alloy the shallow-deep transition occurs; that is, the movement of the conduction band uncovers an impurity level, bringing it into the gap. The response of  $DX$  defects to alloying or pressure is similar, but not identical. We shall focus on the properties of the high-pressure systems, which we simulate here. In particular, the  $DX$  level appears at  $p \geq 22$  kbar for Si, and much earlier, at  $p \geq 9$  kbar for Ge.<sup>9</sup>

Once the  $DX$  level is in the gap, it immediately enters the negative charge state, so that for Si the neutral charge state is not seen under equilibrium conditions, which characterizes the defect<sup>4,10,11</sup> as a negative- $U$  system. For Ge the situation is similar;<sup>5</sup> however, the neutral charge state has been seen in special circumstances.<sup>12,13</sup>

The occurrence of lattice rearrangements around the defect is shown by the existence of different ionization energies, which we list in Table I: the equilibrium emission energy of an electron to the conduction band,  $E_e$ ;

TABLE I. Experimental activation energies (eV) for group-IV impurities in GaAs.  $E_e$  is the thermal ionization energy,  $E_o$  is the optical ionization energy,  $E_c$  is the capture barrier, and  $E_d$  is the donor level position.

Dopant	$E_e$	$E_o$	$E_c$	$E_d$
Si	0.33 <sup>a</sup>	1.44 <sup>b</sup>	0.63 <sup>c</sup>	0.3 <sup>c</sup>
Ge	0.285 <sup>d</sup>			0.104 <sup>d</sup>
Sn	0.07 <sup>c</sup>		0.4 <sup>c</sup>	0.4 <sup>c</sup>

<sup>a</sup>Reference 15.

<sup>b</sup>Reference 16.

<sup>c</sup>Reference 17.

<sup>d</sup>Reference 12.

the nonequilibrium, optical ionization energy<sup>12,14–17</sup> to the conduction band,  $E_o$ ; the capture barrier  $E_c$ , measuring the activation energy for recapture of electrons by the  $DX$  centers, which is at the origin of the PPC,<sup>14,18,19</sup> and finally  $E_d$ , the extrapolated value for zero  $p$  or  $x$  of the  $DX$  level depth from the  $\Gamma$  minimum, as a resonance in the conduction band. The occurrence of PPC for the Ge  $DX$  indicates a nonzero  $E_c$ , although we cannot quote an accepted value; and also, there are no data on the optical ionization energy, to our knowledge.

An important clue to solve the  $DX$  problem emerged from the alloy data: in the alloy the ionization energies  $E_e$  (and  $E_d$ ) are affected by the interaction of the impurity with the Al atoms, and are split in such a fashion as can only be explained<sup>1,20</sup> by a lattice rearrangement that takes the impurity away from the substitutional site towards the interstitial site in a  $C_{3v}$  symmetry, as in Fig. 1.

### III. THE BROKEN-BOND MODEL

In a pioneering work Chadi and Chang (CC) proposed<sup>2</sup> that in fact the *negatively charged defect* underwent a strong symmetry-lowering distortion that took the impurity away from the on-site  $T_d$  configuration along the  $\langle 111 \rangle$  direction to an off-center  $C_{3v}$ -symmetry configuration, which came to be known as the “large lattice relaxation” (LLR) or “broken-bond” configuration (see Fig. 1). The same LLR was also proposed by Dabrowsky and Scheffler<sup>21</sup> for the  $EL2$  defect in GaAs, involving now distortion of the isolated arsenic antisite. The main difference in the energetics of neutral antisite and negative  $DX$  is that while the broken-bond configuration should be stable for  $DX$ , it is metastable for  $As_{Ga}$ . A systematic study of anion antisites then proved that the broken-bond metastability was indeed a common feature for all such impurities, quantitative details depending, however, on the chemical identity of the defect, resulting in quite different energy barriers.<sup>22,23</sup> Further studies of the  $Si_{Ga}$  impurity complicated the theoretical scene, since similar calculations with “slight” technical differences produced results which, while qualitatively similar, diverged in the final comprehension of the model. Exemplifying, we show in Table II results for the energy difference  $E_M$  between the on-site and broken-bond most stable configuration, together with the characteristic impurity displacement,<sup>2,3,6,24</sup> obtained by different authors for the  $Si_{Ga}$  center. Note that the results of CC and

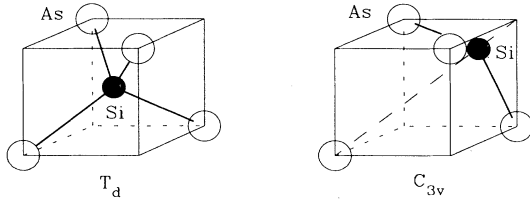


FIG. 1. Scheme of atomic configurations for the  $Si_{Ga}$  defect, undistorted ( $T_d$ ), and when a bond is broken and the impurity is displaced towards the interstitial site ( $C_{3v}$ ).

TABLE II. Results for four different sets of calculations for Si-doped GaAs.  $E_M$  is the energy difference (in eV) between the on-site and broken-bond most stable configuration, with the related displacement (in Å) of the impurity atom.

Calculation	$E_M$	Displacement
CC <sup>a</sup>	-0.22	1.17
DS <sup>b</sup>	0.30	1.36
YSO <sup>c</sup>	-0.65	1.15
SOS <sup>d</sup>	0.27	1.41

<sup>a</sup>Reference 2.

<sup>b</sup>Reference 6.

<sup>c</sup>Reference 3.

<sup>d</sup>Reference 24.

Yamaguchi *et al.* showed the broken-bond configuration for  $Si_{Ga}$  in GaAs to be *metastable* relative to the on-site center.

It is thus important to discuss which points in the broken-bond model are key to the explanation of the experimental data.

The Si impurity substituting for Ga in GaAs carries one extra valence electron, and is most usually understood through the effective-mass (EM) approach,<sup>25</sup> where this extra electron is said to be accommodated in an EM state, which is typically very shallow relative to the conduction-band edge. Theoretically, we may build the EM defect orbital from the lowermost conduction states, and the one-electron level depth relative to the conduction band may be obtained by subjecting an electron in such an orbital to a “hydrogenic” potential screened by the dielectric constant of the host.

On the opposite side we have the “defect molecule” approach, which is better understood starting from any localized basis set, with orbitals centered at the impurity and a few neighboring host atoms. For cation-substitutional group-IV impurities in tetrahedral III-V hosts, the impurity state<sup>26</sup> built from the localized orbitals has  $a_1$  symmetry, and should be singly occupied in the neutral charge state if it falls inside the gap.

These two states (EM and impurity  $a_1$ ) behave very differently with respect to the Mott-Hubbard potential  $U$ , measured by the Fermi-energy region for which a given charge state is detectable in equilibrium conditions. It is known that the magnitude of  $U$  for any impurity depends on the localization of the electronic state, and can be greatly affected by lattice distortions. We can make this explicit by writing the mean-field result<sup>27</sup> as

$$U_{\text{mean-field}} = U_{\text{electronic}} + \Delta U_{\text{rel}}. \quad (1)$$

For a localized impurity orbital associated with a deep electrical level, we may expect a value for the electronic Mott-Hubbard energy  $U_{\text{electronic}}$  around a quarter of an eV, as is the case for the vacancy in Si,<sup>28</sup> the As antisite in GaAs,<sup>21</sup> and so forth. For the EM orbital of shallow donors we should expect  $U_{\text{electronic}}$  to be *almost exactly* zero, since the degree of localization is almost zero: it is built from just a few delocalized band states.

For a shallow donor like GaAs:Si, one then expects from the EM picture that the total energy of the sys-

tem is not affected by the charge state of the center, at least in the  $T_d$  (donor) configuration. That is, if we plot the total energy as a function of distortion for different charge states, at zero distortion the curves should touch, as in Fig. 2. For the PPC effect however, the crossing of the total-energy states  $E(\text{Si}^-)$  and  $E(\text{Si}^+ + 2e_{\text{CB}}^-)$  is the best possible explanation ( $e_{\text{CB}}^-$  denotes an electron in the conduction band). The photoconductivity is observed for Si  $DX$  at  $\sim 1$  eV, corresponding to process  $E_o$  in Fig. 2. After the emission of electrons the system comes back [“along” curve  $E(\text{Si}^+ + 2e_{\text{CB}}^-)$ ] to the  $T_d$  configuration, where it is now precluded from *efficiently* recapturing electrons by the barrier ( $E_c$  in Fig. 2) between the on-site and displaced configurations of the negative charge state. It is then clear that, with  $U_{\text{electronic}}$  zero or close to zero, it is the “camel-back” shape of the curve  $E(DX^-)$  that makes the process occur — and this shape is characteristic of the  $C_{3v}$  distortion, which in turn explains other details in the experimental data, such as the splitting of the deep-level transient spectroscopy (DLTS) peak in Al alloys.

Although this picture is very appealing and reasonable, it is here very important to distinguish between the shallow EM level of  $\text{IV}_{\text{III}}^+$  donors in III-V materials, and the impurity state of these systems. *The EM state is not derived from the localized orbitals of the defect system, and owes its existence to the fact that the donor occupation level  $E(+/0)$  of the impurity lies above the conduction-band minimum.* Since, in this case, the outermost electron of the defect system has a large probability of tunneling to the lower band states, becoming effectively delocalized ( $n$  doping), the ionized-impurity core then deforms the potential around the impurity site, creating the EM potential and concomitantly the EM level. *Once the impurity donor level  $E(+/0)$  enters the gap, this EM level is no longer formed.* The impurity level in the  $T_d$  configuration has been sometimes called the “deep  $A_1$  level” to distinguish it from the broken-bond  $DX$ , and from the EM state.

In the case of  $DX$  centers it is important to note that the impurity captures yet another electron, entering the negative charge state for which the LLR is postulated. In other words, the *acceptor* level  $E(0/-)$  also enters the

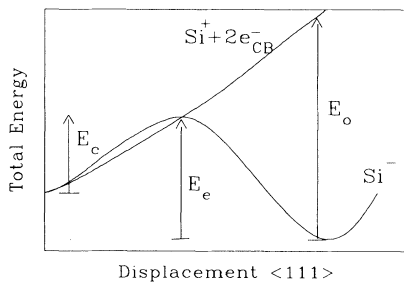


FIG. 2. Total energy for  $\text{Si}_{\text{Ga}}$  as a function of impurity displacement along the  $\langle 111 \rangle$  direction towards the interstitial site, according to the broken-bond model. At zero distortion the curves are aligned by the electronic Mott-Hubbard potential. The characteristic  $DX$ -center activation energies are also indicated.

gap, and, apparently, the neutral charge state is never seen or at least not for  $\text{Si}_{\text{Ga}}$ . This feature typifies a negative- $U$  system (and not a zero- $U$  system, where the three charge states would be equally probable). Since the defect level is in any case already in the gap, the estimate for the Mott-Hubbard  $U$  must be made from realistic localized-defect computations. In the case of  $\text{Si}_{\text{Ga}}$ , the broken-bond model resulted in a negative  $U(0)$  for the neutral charge state in the broken-bond configuration, while for the  $T_d$  site  $U(0)$  is taken to be zero.

Summarizing, the important points explained by the broken-bond model are the following.

- (1) *Shallow-deep transition with alloying/pressure:* The impurity donor level must enter the gap.
- (2) *Simultaneous capture/release of two electrons:* The acceptor level also enters the gap, and the center must have negative  $U$ .
- (3) *Persistent photoconductivity:* There must be a crossing between charge-state energies with relaxation.
- (4) *Large difference between optical and thermal ionization energy:* A LLR must be involved.

Note that, for  $\text{Si}_{\text{Ga}}$ , the particular LLR proposed by CC also explains the splitting of DLTS peaks with alloying. For Ge, items (1), (2), and (3) above are seen, but not, to our knowledge, item (4). Our results indicate, however, that we do not need to invoke the broken-bond model to explain the data, and the fact that item (4) is not detected is probably due to the fact that the impurity does not go off center.

#### IV. DETAILS OF CALCULATIONS

We adopt the supercell approach; that is, we select a cluster of atoms around the defect which we judge representative of the defect potential. This cluster is then repeated in a space-filling mode, satisfying the underlying bulk periodicity so that no surfaces are introduced. The band structure of this *periodic defect crystal* is then self-consistently calculated, within local-density approximation (LDA) with appropriate plane-wave expansions and pseudopotentials. If the cell is large enough so that no interaction between impurities is introduced, the definition of a “gap level” can be easily done since the band structure of the host is still discernible after the folding of the original Brillouin zone (BZ) into the reduced BZ of the defect system, and we may recognize the “defect eigenvalue” as a flat noninteracting band. This is not the case with standard calculations, where a weak interaction between defects, introduced via wave functions, is tolerated for the sake of feasibility and other, more important, convergencies. A defect-band dispersion is thus introduced so that for each nonequivalent  $\mathbf{k}$  point in the BZ we obtain a different eigenvalue. A “defect state” is identified, in any case, by the charge distribution, which shows a localized character. To evaluate the occupation levels of the defect, however, particularly in the case of acceptor levels, Kohn-Sham eigenvalues are not the best estimates<sup>29</sup> and we do not need them if we use total-energy differences for the necessary charge states. This is easily done for supercells in the Zunger and Cohen

scheme of  $\mathbf{k}$  space summation,<sup>30</sup> if we recall that the point-charge potentials are already cancelled out in the  $\mathbf{g}=0$  term, so we must input just a small band-structure correction (evidenced in any change of the valence-band-top eigenvalues) to be able to compare total energies. An occupation level is defined in the usual way:

$$E(0/+) = E(+) - E(0), \quad (2)$$

and here too the total energies are affected by relaxation corrections. We can write  $U_{\text{mean-field}}$  for the neutral state as

$$U_{\text{mean-field}} = E(0/-) - E(+/0) \quad (3)$$

$$= E(+) + E(-) - 2 \times E(0). \quad (4)$$

Apart from Kohn-Sham convergency, the calculation must be converged relative to cell size (in that the defect interaction should not be so large as to interfere with results), and basis set. It is very important to remark that, since we use a self-consistent LDA procedure, the BZ sampling in the sum for the cell electronic density, which is done every cycle, should be very careful, as results may depend critically on the soundness of the density. In particular, unless the defect is extremely localized (inside the “impurity cell”), it can be that the use of the  $\Gamma$  point  $\mathbf{k}=0$  only is insufficient.<sup>31</sup>

We use here a supercell with 54 atoms, with Kleinman-Bylander first-principles pseudopotentials<sup>32,33</sup> including  $l = 2$ , which was found to be very important<sup>23</sup> for these impurities. Kohn-Sham self-consistency was attained through the Car-Parrinello scheme.<sup>34</sup> We include plane waves up to 12 Ry in energy, and the  $\mathbf{k}$  summation is done with the first Chadi-Cohen<sup>35</sup> set (since the 54-atom cell preserves the fcc bravais lattice, the sets comprise two  $\mathbf{k}$  points for  $T_d$  basis symmetry, and five  $\mathbf{k}$  points in  $C_{3v}$  symmetry). Convergence of total-energy differences (between  $T_d$  and  $C_{3v}$  most stable configurations) was checked by increasing the basis up to 16 Ry: results were affected only in the meV range. Our adiabatic total-energy curves are obtained through allowing, at each point in the displacement of the impurity atom, all nearest neighbors to relax. We do not allow all atoms to relax in order to avoid strenghtening the defect interactions. The remaining forces on the other neighbors are however calculated, and are negligible (of the order of  $0.004 \text{ eV}/\text{\AA}$ ); if this were not the case, a larger supercell would be recommended. Pressure effects are introduced through the lattice constant in a thoroughly consistent way. We first obtain the equilibrium lattice constant for our theoretical GaAs crystal ( $5.58 \text{ \AA}$  in a two atom supercell with plane waves up to 15 Ry and two  $\mathbf{k}$  points;  $5.57 \text{ \AA}$  in the supercell with the defect-calculation setup). We then calculate the bulk modulus in the quadratic approximation; next, with the help of the modulus, we calculate the lattice constant under a given pressure. *No reference is taken from experimental data in this case.* This is an important detail when dealing with these shallow donor impurities, since it is quite probable that conduction-band states interfere with defect states, which is even more crucial due to defect-band dispersion. We work always under high ( $\sim 30 \text{ kbar}$ ) pressure in order to get rid

of band states: the lowest conduction state eigenvalue for this pressure appears, in our calculations, at  $\geq 1.6 \text{ eV}$ , which allows for a clear distinction between defect and bulk states.

## V. RESULTS AND DISCUSSION

The substitutional Ge impurity, as expected, introduces a localized  $a_1$  antibonding state in the gap region. We show in Fig. 3(a) the charge contour plot for the doubly occupied state in the  $T_d$  site: this contour is quite typical of such impurities, and its almost “didactical” antibonding character plays an important role when considering lattice relaxations (already included in the contours). In the case of Ge, with a covalent radius very close to that of Ga, the effect of the antibonding charge

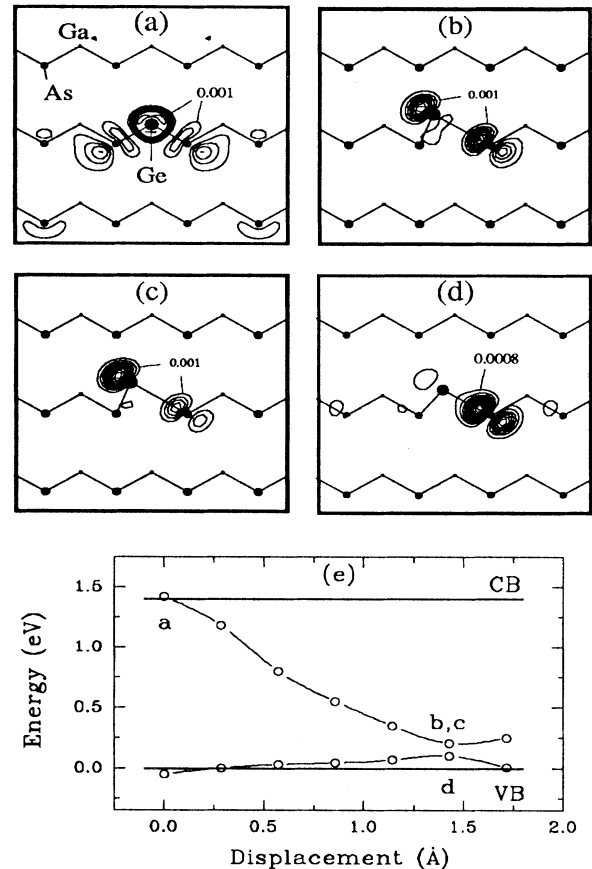


FIG. 3. Charge densities, in electrons per unit cell, for the doubly occupied  $a_1$  state for the  $\text{Ge}_{\text{Ga}}$  defect: (a) highest occupied impurity level in  $T_d$  symmetry, obtained through a calculation using only the  $\Gamma$  point; (b) same as (a), in  $C_{3v}$  symmetry; (c) same as (b) using the Chadi-Cohen special set of  $\mathbf{k}$  points; (d) deep-level  $a_1$  resonance in the valence band, which interacts with the gap state; and (e) eigenstate interactions, for near gap eigenvalues, for displacement of impurity in the  $\langle 111 \rangle$  direction [the labeling here links the eigenvalue to the corresponding charge density (a) to (d) above]. Note the high degree of localization of all states depicted.

density of this state actually dictates the motion of the defect system. It is also worth noting that the localization of the charge density is quite high, and so the level will be coupled to any  $a_1$  localized resonances in the valence band, as we will see. As we pull the Ge atom along the  $C_{3v}$  path of the LLR proposed for  $DX$ 's, this orbital evolves and we show in Fig. 3(b) the charge distribution for the local minimum of the broken-bond configuration, obtained through a calculation using one  $\mathbf{k}$  point ( $\Gamma$  point) in the BZ summation.<sup>36</sup> We see the dangling-bond-like density centered on the As neighbor, with some tail on the impurity. This charge distribution is the key to the stability of the broken-bond configuration, since the saturated dangling bond is very stable. This picture changes however when we augment the sampling of the BZ, and we show in Fig. 3(c) the charge density for the same state, using the Chadi-Cohen set. Now the state is more localized around the impurity, and there is less charge for this state around the dangling bond on the As neighbor. Due to the antibonding character of the state, this situation is less stable than what we are led to believe when using only the  $\Gamma$  point; that is, the  $\Gamma$ -point sampling gives an unrealistic description of the situation.

In fact, we retrieve the dangling-bond-like electrons in another  $a_1$  state which interacts with the gap state<sup>37</sup> along the  $C_{3v}$  motion [see Figs. 3(d) and 3(e)]. In spite of the fact that this localized state is part of a resonance at the top of the valence band, the situation is still less stable than that of the  $T_d$  site, as we see next.

We show in Fig. 4 the adiabatic total-energy curve obtained for the negative Ge impurity, for displacement along the  $\langle 111 \rangle$  direction towards the interstitial site. Dashed lines refer to our previous calculations,<sup>36</sup> which were done taking the  $\Gamma$ -point approximation for the sum in the electronic density, and relate to the density contour of Fig. 3(b). We can see the effect of the different charge density on the total energies for the same configuration: if qualitatively we still have the same metastability effect, *since the metastable energy is now so much higher than the  $T_d$ -site energy, we have no reason to expect, for the  $Ge_{Ga}$  impurity, any  $C_{3v}$  distortion similar to that proposed for  $Si_{Ga}$ .* This is not surprising in

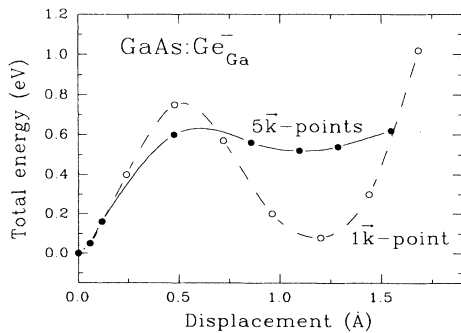


FIG. 4. Total energy for the negative  $Ge_{Ga}$  defect as a function of displacement of the impurity along the  $\langle 111 \rangle$  direction. The dashed line is the calculation using only the  $\Gamma$  point, and the solid line is the result with Chadi-Cohen special set of  $k$  points.

view of the fact that the As antisite, which is the core of the  $EL2$  defect and which is really much more similar to the Ge  $DX$ , actually goes off center only through photoexcitation,<sup>21,23,38</sup> as recently and clearly detected in positron-annihilation studies.<sup>39</sup>

We thus return to the results for the  $T_d$ -symmetric defect, and at this step, to get a better view of the relaxation processes, we first allow no relaxation of the neighbors. We obtain as a first result the location of the electronic ionization levels for the impurity: At this value of pressure ( $\sim 30$  kbar) both donor and acceptor levels appear in the gap, so that the capture of two electrons would be allowed. Our result for the electronic  $U$  is indicative of the similarity between impurity and host atoms, being small, and positive ( $U_{\text{electronic}} \sim 0.1$  eV). The obtained value for  $U$  is already at the limit of accuracy for our calculations, and we estimate, from results on  $Si_{Ga}$  (Ref. 40) obtained through the same systematics, that  $U$  here may be underestimated by  $\sim 0.05$  to  $0.1$  eV.

A result that can be checked straightforwardly with experiment is that *the acceptor level is already, even without relaxations, lower than that of  $Si_{Ga}$  (Ref. 40) and so should enter the gap at lower pressures, as actually detected.* The fact that the Ge donor level is lower than that of Si or Sn is seen also for these impurities in GaP.<sup>41</sup>

Next we show, in Fig. 5, the total-energy curves for the *tetrahedral configuration* of the Ge impurity system, in the neutral, positive, and negative charge states of the defect center (the system is always neutral). Now the relaxation is along the breathing mode. The curves are aligned through the calculated  $U_{\text{electronic}}$ , at zero relaxation, according to the following ansatz: under equilibrium conditions, supposing a reservoir  $R$  that can hold or release electrons, when

$$E[R^- + D^+] = E[R^0 + D^0] \text{ then } \mu = E_D(+/0), \quad (5)$$

and when

$$E[R^+ + D^-] = E[R^0 + D^0] \text{ then } \mu = E_A(0/-), \quad (6)$$

where  $D$  stands for defect center. In this case, for the

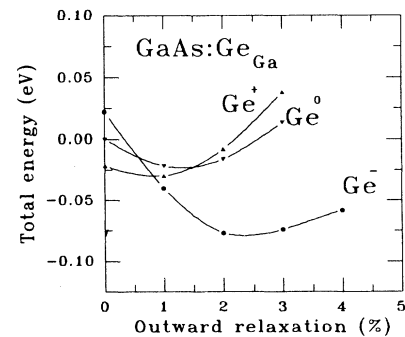


FIG. 5. Total energy as a function of breathing-mode relaxations for the  $Ge_{Ga}$  impurity in tetrahedral configuration. The curves are aligned through the calculated  $U_{\text{electronic}}$  at zero relaxation.

limiting energies,  $E[R^+ + D^-] = E[R^- + D^+] + U$ .

As a first result we find that, *at this value of pressure, allowing for symmetrical relaxations, the Ge impurity is a negative- $U$  system.* Furthermore, there is a crossing point between the positive and negative charge state total energies; so, *for the Ge impurity, the PPC effect may result from breathing relaxations,* not involving a LLR in the broken-bond sense.

In a recent investigation by Baj and co-workers<sup>42,43</sup> the value of  $U$  for  $\text{Ge}_{\text{Ga}}$  was obtained through Hall mobility measurements under pressure. The authors extract a positive  $U$  of 32 meV at zero pressure, with pressure coefficients for the donor and acceptor levels that would indicate a crossing point from positive to negative  $U$ , but only at very high pressures (at 30 kbar,  $U$  would be around  $-10$  meV). However, the authors assumed for the calculations the usual trigonal model for the two-electron center (fourfold degeneracy of the negatively charged state). If instead an  $A_1$ -symmetric state is assumed, the value for  $U$  at zero pressure decreases to 20 meV,<sup>44</sup> implying that a crossing to negative  $U$  is possible at lower values of pressure around 13 kbar.

Other groups<sup>12,13</sup> working with highly Ge-doped GaAs at very low temperatures and at pressures lower than 12 kbar, that is, actually in a region where the impurity levels are already in the gap but  $U$  is at the limit between positive and negative values, seem to detect the neutral and negative charge states at the same time, while yet other experiments done under higher pressures<sup>5</sup> detect already the negative- $U$  character of the impurity.

These results seem to be reasonably well described by the breathing-mode relaxations of the Ge neighbors in  $T_d$  symmetry. We do not study the impurity system under low pressure, due to the already discussed difficulties in dealing with band states. Thus, we do not extract a value for the pressure dependence of the donor/acceptor levels. We point out, however, that our result for the absolute value of  $U$  (between  $\sim 50$  and 100 meV) at 30 kbar is of the same order of magnitude and sign as the experimental estimate; this is also a strong argument for the breathing-mode model since, if the broken-bond model is invoked, we might expect a much larger absolute value for  $U$  (since

the curve for the system  $[R^- + D^+]$  rises steeply with  $C_{3v}$  distortion).

## VI. SUMMARY AND CONCLUSIONS

Summarizing, we find that the cation-substitutional Ge impurity in GaAs behaves, as expected, as a shallow donor in normal conditions. At the same time, the impurity states present a localized and almost didactical antibonding character so that, once the donor occupation level moves into the gap, the center behaves as a deep-level defect. The shallow-deep transition should for Ge occur at lower pressures than for Si. We find a positive but small value for the Mott-Hubbard *electronic*  $U$ , so that with zero distortion (before capturing an electron for which there exists a small barrier) the total  $U$  is actually positive.

We further find that bond-breaking distortions are not energetically favored, and the usual  $C_{3v}$  configuration invoked to explain the experimental data for  $DX$  centers is metastable for the negatively charged center. Our results indicate, however, that symmetric *breathing-mode* distortions, driven by the antibonding character of the wave functions, can explain the known data in a very similar but simpler model: Our configuration-coordinate model can explain both the PPC effect at high pressures and the anomalous behavior of the Mott-Hubbard  $U$  near the shallow-deep transition point.

Further experimental work on this impurity should include positron annihilation studies: from our results we expect that, in contrast to the  $EL2$  defect where the central antisite leaves behind a volume comparable to the vacancy, in the case of Ge no "empty volume" should be found even for conditions where negative- $U$  behavior is detected.

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<sup>1</sup> P. M. Mooney, J. Appl. Phys. **67**, R1 (1990).

<sup>2</sup> D. J. Chadi and K. J. Chang, Phys. Rev. Lett. **61**, 873 (1988); Phys. Rev. B **39**, 10 063 (1989).

<sup>3</sup> J. Dabrowski and M. Scheffler, Mater. Sci. Forum **83-87**, 735 (1991).

<sup>4</sup> T. N. Theis, P. M. Mooney, and B. D. Parker, J. Electron. Mater. **20**, 35 (1991).

<sup>5</sup> T. Fujisawa, J. Yoshino, and H. Kukimoto, Jpn. J. Appl. Phys. **29**, L388 (1990).

<sup>6</sup> E. Yamaguchi, K. Shiraishi, and T. Ohno, J. Phys. Soc. Jpn. **60**, 3093 (1991).

<sup>7</sup> M. Saito and A. Oshiyama, Mod. Phys. Lett. B **7**, 1567

(1993).

<sup>8</sup> R. Jones and S. Öberg, Phys. Rev. B **44**, 3407 (1991).

<sup>9</sup> J. E. Dmochowski, P. D. Wang, and R. A. Stradling, in *The 20th International Conference on the Physics of Semiconductors, Thessaloniki, Greece, 1990*, edited by E. M. Anastassakis and J. D. Joannopoulos (World Scientific, Singapore, 1990), Vol. I, p. 658.

<sup>10</sup> V. Mosser, S. Contreras, J. L. Robert, R. Piotrkowski, W. Zawadzki, and J. F. Rochette, Phys. Rev. Lett. **66**, 1737 (1991).

<sup>11</sup> S. Ghosh and V. Kumar, Phys. Rev. B **46**, 7533 (1992).

<sup>12</sup> P. J. van der Well, P. Wisniewski, R. Suski, J. Singleton, C. Skierbiszewski, L. J. Giling, R. Warburton, P. J. Walker, N. J. Mason, R. J. Nicholas, and M. Eremets, J. Phys. Condens. Matter **5**, 5001 (1993).

- <sup>13</sup> C. Skierbiszewski, T. Suski, P. Wisnienski, W. Jantsch, G. Ostermayer, Z. Wilamowski, P. G. Walker, N. J. Mason, and J. Singleton, *Appl. Phys. Lett.* **63**, 3209 (1993).
- <sup>14</sup> D. V. Lang and R. A. Logan, *Phys. Rev. B* **19**, 1015 (1979).
- <sup>15</sup> O. Kumagai, H. Kawai, Y. Mori, and K. Kaneko, *Appl. Phys. Lett.* **45**, 1322 (1984).
- <sup>16</sup> M. F. Li, P. Y. Yu, E. R. Weber, and W. Hansen, *Phys. Rev. B* **36**, 4531 (1987).
- <sup>17</sup> T. Suski, P. Wisniewski, C. Skierbiszewski, L. H. Dmowski, P. J. van der Well, J. Singleton, L. J. Giling, and J. J. Harris, *J. Appl. Phys.* **69**, 3087 (1991).
- <sup>18</sup> M. Tachikawa, T. Fujisawa, H. Kukimoto, A. Shibata, G. Oomi, and S. Minomura, *Jpn. J. Appl. Phys.* **24**, L893 (1985).
- <sup>19</sup> A. Dissanayake, M. Elahi, H. X. Jiang, and J. Y. Lin, *Phys. Rev. B* **45**, 13996 (1992).
- <sup>20</sup> T. N. Morgan, *Phys. Rev. B* **34**, 2664 (1986).
- <sup>21</sup> J. Dabrowski and M. Scheffler, *Phys. Rev. Lett.* **60**, 2183 (1988).
- <sup>22</sup> M. J. Caldas, A. Fazzio, J. Dabrowski, and M. Scheffler, *Int. J. Quantum Chem. Symp.* **24**, 563 (1990).
- <sup>23</sup> M. J. Caldas, J. Dabrowski, A. Fazzio, and M. Scheffler, *Phys. Rev. Lett.* **65**, 2046 (1990).
- <sup>24</sup> M. Saito, A. Oshiyama, and O. Sugino, *Phys. Rev. B* **47**, 13205 (1993).
- <sup>25</sup> S. T. Pantelides and C. T. Sah, *Phys. Rev. B* **10**, 638 (1974).
- <sup>26</sup> T. M. Schmidt and A. Fazzio, *Solid State Commun.* **82**, 83 (1992).
- <sup>27</sup> A. Fazzio, M. J. Caldas, and A. Zunger, *Phys. Rev. B* **30**, 3430 (1984).
- <sup>28</sup> J. Bourgoin and M. Lannoo, in *Point Defects in Semiconductors I*, edited by M. Cardona, Springer Series in Solid State Sciences Vol. 22 (Springer-Verlag, New York, 1981).
- <sup>29</sup> Eigenvalues of virtual states carry no physical meaning, neither in Hartree-Fock nor in local-density formalisms, see J. C. Slater, in *The Self-Consistent Field for Molecules and Solids Vol. IV*, edited by L. I. Schiff (McGraw-Hill, New York, 1974.)
- <sup>30</sup> J. Ihm, A. Zunger, and M. L. Cohen, *J. Phys. C* **12**, 4409 (1979).
- <sup>31</sup> J. Furthmüller and M. Fähnle, *Phys. Rev. B* **46**, 3839 (1992).
- <sup>32</sup> L. Kleinman and D. M. Bylander, *Phys. Rev. Lett.* **48**, 1425 (1982).
- <sup>33</sup> R. S. Stumpf, X. Gonze, and M. Scheffler (unpublished).
- <sup>34</sup> R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).
- <sup>35</sup> D. J. Chadi and M. L. Cohen, *Phys. Rev. B* **8**, 5747 (1973).
- <sup>36</sup> A. Fazzio, T. M. Schmidt, P. P. M. Venezuela, and M. J. Caldas, in *Physics of Semiconductors: Proceedings of the XXI International Conference, Beijing, China, 1992*, edited by Ping Jiang and Hon-Zhi Zheng (World Scientific, Singapore, 1993), Vols. 1 and 2, p. 1713.
- <sup>37</sup> A. Fazzio, P. P. M. Venezuela, and T. M. Schmidt, *Mater. Sci. Forum* **143-147**, 991 (1994).
- <sup>38</sup> M. J. Caldas and E. Molinari, *Solid State Commun.* **89**, 493 (1994).
- <sup>39</sup> K. Saarinen, S. Kuisma, P. Hautojärvi, C. Corbel, and C. LeBerre, *Phys. Rev. B* **49**, 8005 (1994).
- <sup>40</sup> T. M. Schmidt, M. J. Caldas, and A. Fazzio (unpublished).
- <sup>41</sup> F. Mehran, T. N. Morgan, R. S. Title, and S. E. Blum, *Solid State Commun.* **11**, 661 (1972).
- <sup>42</sup> M. Baj, L. H. Dmowski, T. Slupiński, and D. Wasik, *Mater. Sci. Forum* **143-147**, 1019 (1994).
- <sup>43</sup> M. Baj, L. M. Dmowski, and T. Slupiński, *Phys. Rev. Lett.* **71**, 3529 (1993).
- <sup>44</sup> M. Baj (private communication).