

## Microscopic picture of the single vacancy in germanium

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A complete microscopic picture of the germanium vacancy is presented, and our results are compared with recent measurements. We analyze, through first principles calculations, the structural relaxations, Jahn-Teller distortions, and orbitals for the charge states  $(++, +, 0, -, --)$ . The formation energies for the different charge states are presented, as well as the positions of the  $(+++)$ ,  $(+/0)$ ,  $(0/-)$ , and  $(-/-)$  levels, and we obtain that the vacancy in Ge is not an Anderson negative- $U$  system, as opposed to the silicon vacancy. We propose as an explanation a much smaller electron-lattice coupling for the  $E$  mode in germanium than in silicon.

In the early 1980s the experimental group from Lehigh University<sup>1</sup> and the theoretical group from Bell Laboratories<sup>2</sup> gave us a complete understanding of the microscopic picture of the silicon vacancy, which is today often referred to as the ‘‘Watkins model.’’ This very simple defect, the lack of a silicon atom in the regular crystal lattice, has an important influence over the electrical and optical properties of the material. Despite its simplicity, this defect presents a rich variety of interesting physical properties, such as (i) several charge states in the gap; (ii) different local lattice relaxations for different charge states; (iii) the charge states  $(0)$ ,  $(+)$ , and  $(++)$  forming an Anderson negative- $U$  system,<sup>3</sup> with the  $(+)$  state being a missing (metastable) state.

Curiously enough, in contrast to the silicon case, there is no complete microscopic picture for the germanium vacancy. The main reason for this disparity between silicon and germanium is that most of the experimental knowledge on silicon vacancy came from electron paramagnetic resonance measurements, which had very limited success when applied to germanium. However, recent perturbed angular correlation spectroscopy (PAC) measurements<sup>4,5</sup> were able to provide some new microscopic information about the germanium vacancy. In the PAC experiments, point defects produced by electron irradiation are trapped at <sup>111</sup>In probes, and their properties are studied as a function of the Fermi level. The authors obtained that the vacancy  $(0/-)$  level should be somewhere between 0.16 and 0.24 eV above the top of the valence band.<sup>4,5</sup> In another set of experiments, the same group<sup>6</sup> used a combination of two different techniques, deep level transient spectroscopy (DLTS) and PAC, to obtain information about deep level defects in germanium. With the DLTS they were able to detect a level at 0.33 eV above the top of the valence band, and through the PAC measurements they identified that this level was related to a neutral mono-vacancy.

These experimental results have motivated us to perform an extensive theoretical study on the germanium vacancy. We report, using first principles calculations, results for the charge states  $(++)$ ,  $(+)$ ,  $(0)$ ,  $(-)$ , and  $(--)$ , their local atomic distortions, orbitals, and formation energies. We also

calculate the  $(+++)$ ,  $(+/0)$ ,  $(0/-)$ , and  $(-/-)$  defect transition energy levels. Our main results are (i) all the lattice distortions in germanium are similar to the distortions in silicon, in the sense that the local symmetries around the vacancy, for the lowest energy structures, are the same in germanium and in silicon for all charge states; (ii) except for the  $(++)$  charge state, the magnitudes of the distortions are smaller in germanium than in silicon;<sup>7</sup> (iii) we find that germanium is *not* an Anderson negative- $U$  system for any charge state. This is related to item (ii) above, as will be discussed below.

We have performed total energy *ab initio* calculations based on the density functional theory, with the local density approximation for the exchange-correlation potential.<sup>8</sup> To describe the vacancy we have used a supercell approach with 128 atoms in the unit cell. Norm-conserving pseudopotentials of Bachelet, Hamann, and Schlüter,<sup>9</sup> in the Kleinman-Bylander<sup>10</sup> form, were used. A plane wave basis set expansion up to 12 Ry of energy cutoff was used, and the Brillouin zone was sampled using the  $\Gamma$  point.<sup>11</sup> This size of supercell and number of  $\mathbf{k}$  points used were shown to give reasonable results for the silicon vacancy.<sup>7</sup> All the studied systems have been relaxed without any symmetry until all components of the forces were smaller than 0.0005 hartree/a.u. For the calculations with the vacancy in charge state  $q$ , a uniform charge density of  $\rho = -q/\Omega_{cell}$  is added to the unit cell of volume  $\Omega_{cell}$ . This ensures that the whole system is charge neutral. The formation energy of a vacancy in charge state  $q$ ,  $E_q^V(\mu_e)$  is calculated in the supercell approximation as

$$E_q^V(\mu_e) = E_q^{N-1} + q(\mu_e + E_v) - \frac{N-1}{N} E^N, \quad (1)$$

where  $E^{N-1}$  is the total energy of the supercell with a vacancy in charge state  $q$  ( $N-1$  atoms),  $E^N$  is the total energy of the perfect lattice supercell ( $N$  atoms), and  $\mu_e$  is the position of the Fermi level relative to the top of the valence band  $E_v$ . The top of the valence band has been corrected in

TABLE I. Interatomic distances (in Å) between the four nearest-neighbor atoms to the vacancy site, for the different vacancy charge states  $q$ . For the bulk, all the distances are the same and equal to 3.96 Å. The relative volume change  $V_{rel}^i = 100(V - V_0)/V_0$ ,  $i = \text{Ge}$  or  $\text{Si}$ , is also presented.  $V$  and  $V_0$  are calculated as the volumes of the tetrahedra formed by the four nearest-neighbor atoms of the relaxed and ideal vacancy, respectively. The results for Si are from Ref. 7 (we report their numbers for a cell with 216 sites).

$q$	$d_{12}$	$d_{13}$	$d_{14}$	$d_{23}$	$d_{24}$	$d_{34}$	$V_{rel}^{\text{Ge}}$	$V_{rel}^{\text{Si}}$
(++)	3.57	3.57	3.57	3.57	3.57	3.57	-26.7	-26.1
(+)	3.44	3.55	3.54	3.55	3.54	3.44	-30.3	-39.4
(0)	3.40	3.55	3.54	3.55	3.54	3.40	-31.2	-42.4
(-)	3.38	3.37	3.37	3.37	3.37	3.14	-40.4	-55.0
(--)	3.36	3.36	3.36	3.36	3.36	3.24	-40.8	-51.9

the defect supercells by the average potential around the furthest interstitial from the vacancy site.<sup>12</sup>

In Table I we present our results for the lattice relaxations and distortions. For each charge state we present the six interatomic distances between the four nearest-neighbor atoms to the vacancy site.<sup>13</sup> In the perfect crystal all these six interatomic distances are the same and equal to 3.96 Å. For the charge state (++) we obtain an inward relaxation with a volume change relative to the perfect lattice of approximately 27%. All of the six interatomic distances are equal, which indicates that the point-group symmetry around the vacancy site is  $T_d$ . This result is the same as in silicon. A calculation<sup>7</sup> for silicon performed with a supercell with 216 sites obtained a similar inward relaxation (see Table I). However, the same authors obtained an outward relaxation with a supercell of 128 sites. We did not find such an outward relaxation, and when we embed our 128 supercell in a 216 supercell, and repeat the calculation without further atomic relaxation, we find that all the components of the forces are smaller than 0.003 hartree/a.u. This indicates that the atomic displacements for the germanium vacancy are well represented in a supercell with 128 atomic sites.

With the addition of an electron to the triply degenerate orbitals, i.e., the (+) state, we obtain a lattice distortion with two equal and shorter interatomic distances, and four approximately equal and longer distances. This is also similar to what happens in the silicon vacancy case, and characterizes a  $D_{2d}$ -point symmetry. The volume change also characterizes an inward relaxation, with a contraction of approximately 30% when compared to the unrelaxed structure. The addition of another electron takes the system to the (0) charge state, and we also obtain a  $D_{2d}$  symmetry, as expected, with four longer bonds and two shorter ones. However, the distortions in the (+) and (0) charge states in germanium are *smaller* than in silicon. A decomposition in symmetrized coordinates shows that the Jahn-Teller distortions, i.e., distortions that will induce a reduction to the  $D_{2d}$  point group symmetry, are approximately 3 times smaller in germanium than in silicon. This implies a stronger Jahn-Teller coupling in silicon than in germanium. This weaker coupling to the lattice in germanium tends to destabilize the negative- $U$  system for the (++) , (+) , (0) charge states, and this is precisely what we obtain, as will be shown later.

Moving now to the (-) state, there is another Jahn-Teller

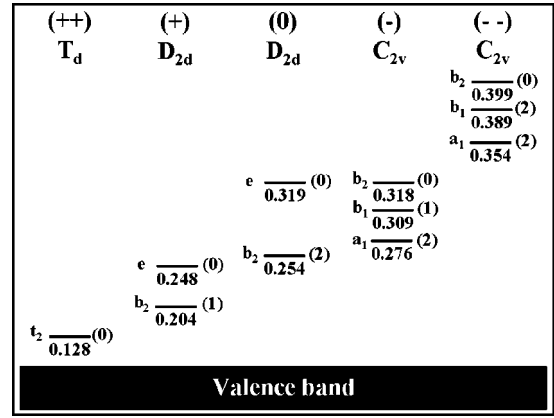


FIG. 1. The single-particle energy levels obtained from the LDA calculation for each charge state. For each level it is given (1) its symmetry, shown on its left; (2) its occupation, shown on its right, in parentheses; (3) its position, in eV, with respect to the valence band maximum [corrected in each case as described in the text (Ref. 12)], shown below it. The charge states and the point-symmetry groups around the vacancy are presented at the top of the figure.

distortion, and the point-group symmetry becomes  $C_{2v}$ , which is again similar to the  $V_{Si}$ . There is still a further inward relaxation, with a relative volume change with respect to the undistorted lattice of 40%. Finally, in the (--) state the point-group symmetry is also  $C_{2v}$ , and the lattice distortions are very similar to the ones obtained for the (-) state. Once more this behavior is similar to what is observed for the silicon vacancy. Therefore, as far as the point-group symmetries are concerned, the germanium vacancy behaves exactly as the silicon vacancy.

In Fig. 1 we present the germanium vacancy levels which are localized in the gap, for each charge state. They are the Kohn-Sham eigenvalues measured with respect to the valence band maximum (as mentioned previously, the valence band maximum has been corrected for each charge state<sup>12</sup>). All the orbitals degeneracies are consistent with the point-group symmetries discussed above. For each one of the orbitals, we plot in Fig. 2 the charge densities along the [110] (shown on the left) and  $[1\bar{1}0]$  (shown on the right) planes. We also indicate the orbitals symmetries. Whenever there is orbital degeneracy, the plotted charge density is the sum of the charge densities for the degenerate orbitals. The site shown in black represents the vacancy. The sites in pink mark the positions of the unrelaxed nearest-neighbor atoms to the vacancy, and red and yellow sites are the positions of the relaxed nearest-neighbor atoms to the vacancy. Only in the (-) and (--) states can the pink sites be clearly distinguished from the red and yellow sites. The blue sites mark the position of other germanium atoms. As can be seen from Fig. 2, the modifications in the orbitals upon each change in charge states are small. One should also note that the  $b_2$  orbitals in the charge states with  $D_{2d}$  point-group symmetry [(+) and (0)], and the  $a_1$  orbitals in the charge states with  $C_{2v}$  point-group symmetry [(-) and (--)] are more delocalized than the  $e$  orbitals ( $D_{2d}$ ) and  $b_1$  and  $b_2$  orbitals ( $C_{2v}$ ). The bonding character of all the orbitals are similar to the bonding character of the orbitals in silicon.<sup>14</sup>

In Fig. 3 we present the vacancy formation energies for each charge state  $q$ , as a function of the Fermi level  $\mu_e$ ,

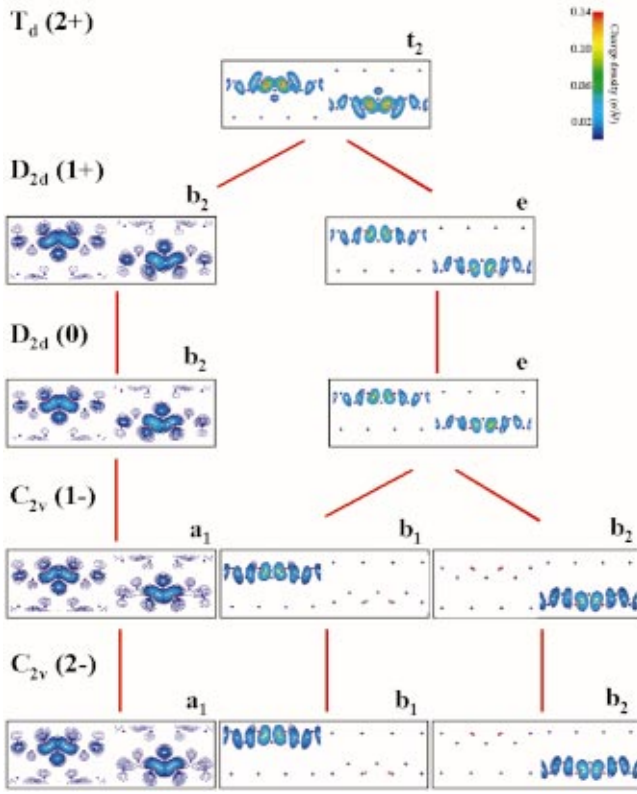


FIG. 2. (Color) Contour plots of the charge densities along the  $[110]$  (left) and  $[1\bar{1}0]$  (right) planes. The plots are for the vacancy levels in the gap shown in Fig. 1, for each charge state. The point-group symmetry for each charge state, as well as the orbitals symmetries, are also indicated. The color codes are explained in the text.

obtained using Eq. (1). Comparison with the results for silicon show that the formation energies are significantly smaller in germanium than in silicon, for all charge states, which makes the vacancy much more important for self-diffusion in germanium than in silicon.<sup>15</sup> Our numbers for the formation energies are in good agreement with the experimental results, which for the singly charged negative vacancy range from 1.7 to about 2 eV,<sup>16</sup> whereas we obtain 2.3 eV.

From the curves of Fig. 3 we obtained the ionization levels, i.e., the values of the Fermi level  $\mu_e$  where the formation

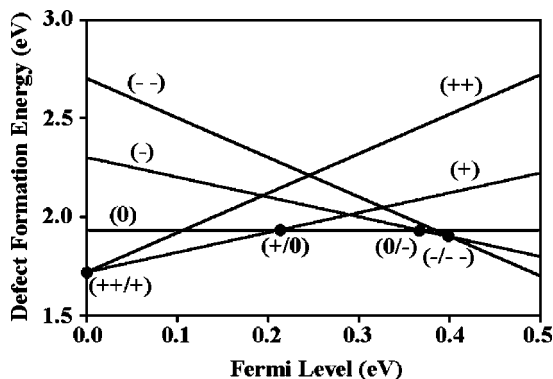


FIG. 3. Formation energies for the different charge states as a function of the Fermi energy. The ionization levels are marked with solid dots.

energies of two charge states become equal. These values are indicated in Fig. 3 with black dots. The most important point is that the  $(++)$ ,  $(+)$ ,  $(0)$  states *do not* form an Anderson negative- $U$  system. From our results we obtain  $U=0.21$  eV,<sup>17</sup> and using numbers of Puska *et al.* (for a 216 sites supercell) we obtain  $U=-0.12$  eV.

Haeslelein *et al.*<sup>5</sup> placed the  $(0/-)$  level at  $0.20 \pm 0.04$  eV above the top of the valence band using PAC. The DLTS results of Zistl *et al.*<sup>6</sup> find a level at 0.33 eV above the top of the valence band, and if this level is also associated with the  $(0/-)$  transition, we can infer that it is between 0.20 and 0.33 eV. We obtain for this level a value of 0.37 eV, which is not far from the 0.33 eV obtained from the DLTS measurements. However, given the large spin-orbit splitoff of the valence band in Ge, and the fact that we do not include spin-orbit effects in our calculations, it is hard to compare the absolute position of our calculated levels with the experimental results.

It remains as an important question why in germanium the charge states  $(++)$ ,  $(+)$ , and  $(0)$  *do not* form an Anderson negative- $U$  system, whereas in silicon they do. The total energy  $E^q$  for a given charge state  $q$  can be written as<sup>2,3,14</sup> a function of the normal modes<sup>18</sup>  $Q_{\Gamma_i}$  ( $\Gamma_i=A_1$  or  $E$ ), expanded up to second order around the coordinates of the undistorted lattice as

$$E^q(Q_{\Gamma_i}) = E_v^q + \sum_{\Gamma_i} \left[ \frac{1}{2} k_{\Gamma_i}^q Q_{\Gamma_i}^2 - \lambda_{\Gamma_i}^q Q_{\Gamma_i} \right], \quad (2)$$

where  $E_v^q$  are the vertical (i.e., without any lattice relaxation or distortion) shifts in the total energies,  $\lambda_{\Gamma_i}^q$  are the electron-lattice coupling coefficients, and the  $k_{\Gamma_i}^q$  are the force constants. The energy gain, for each normal mode and for each charge state, upon lattice relaxation or distortion is given by

$$\Delta E_{\Gamma_i}^q = - \frac{(\lambda_{\Gamma_i}^q)^2}{2k_{\Gamma_i}^q}. \quad (3)$$

Using the above equations, we can write  $U$  as<sup>17</sup>  $U = U_v + U_{A_1} + U_E$ , where  $U_v$  is the contribution coming from the vertical shifts,  $U_{A_1}$  is the contribution coming from the energy gains associated with the  $A_1$  mode, and  $U_E$  is the contribution from the energy gains due to the  $E$  mode (Jahn-Teller energy gains). For silicon we estimate<sup>7,14</sup>  $U_v=0.4$  eV,  $U_{A_1}=-0.3$  eV, and  $U_E=-0.2$  eV. Using the numbers for silicon,<sup>7,14</sup> the relative distortions in germanium and silicon for each normal mode, and the ratio between the atomic masses and the ratio between the phonon modes in silicon and germanium, we estimate for germanium  $U_{A_1}=-0.2$  eV and  $U_E=-0.01$  eV. We calculated for germanium  $U_v=0.4$  eV, which gives  $U=0.19$  eV, very similar to the value of  $U=0.2$  eV that we had obtained using our results for the formation energies. What these numbers show is that the contribution to the  $U$  due to the breathing mode ( $U_{A_1}$ ) is similar in both silicon and germanium, but the contribution due to the Jahn-Teller distortion ( $U_E$ ) is *much smaller* in germa-

nium than in silicon. The reason is an electron-lattice coupling  $\lambda_{\frac{q}{E}}$  in germanium that is about six times smaller than in silicon.<sup>19</sup>

In summary, we have presented a complete microscopic picture of the germanium vacancy (lattice distortions, charge distributions, formation energies, and ionization levels). Our results for ionization levels are in fair agreement with recent

experiments.<sup>4-6</sup> In contrast to the silicon vacancy, the germanium vacancy does not present a negative- $U$  due to a small electron-lattice coupling for the  $E$  mode.

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