

Self-interstitial defect in germanium

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Electronic and structural properties of a self-interstitial defect in Ge are studied through first-principles calculations. As in Si, the lowest-energy configuration is the $\langle 110 \rangle$ dumbbell. However, the defect in Ge seems to involve four rather than just two atoms, and we propose to call it a kite defect. The formation energy for the interstitial at a hexagonal site is significantly higher in Ge when compared to Si, which may help to explain why in Ge only the vacancy contributes to self-diffusion. An interpretation of recent perturbed angular correlation spectroscopy results is also presented.

During the first years of research in the field of semiconductor physics both germanium and silicon attracted a lot of attention. However, as time went by, only silicon survived as a viable material for electronic devices. This led to a much greater understanding of its properties, including its intrinsic defects like vacancies and self-interstitials.¹⁻⁵ However, the recent interest in Si/Ge alloys and heterostructures has brought Ge again to the spotlight.⁶ In a recent experiment, using perturbed angular correlation (PAC) spectroscopy, Haesslein *et al.*⁷ were able to provide new microscopic information about intrinsic defects in germanium. The PAC experiment detected two point defects produced by electron irradiation trapped at ¹¹¹In probes, and their properties are studied as a function of the electronic chemical potential. One of them was identified with great confidence as a single vacancy. The second observed defect has been tentatively assigned as a germanium self-interstitial. The dependence of the results on the chemical potential led the authors to propose that the interstitial (+/0) ionization level should be located somewhere between 0.02 and 0.06 eV below the bottom of the conduction band.

In a previous paper we have presented a complete microscopic picture of the germanium single vacancy.⁸ In the present report we make a detailed study of the self-interstitial defect in germanium, completing in this way the theoretical analysis of elementary intrinsic defects in Ge and of the PAC experiments. Previous work on the Si self-interstitial has shown that the $\langle 110 \rangle$ -split dumbbell is the lowest-energy configuration, followed by the Si interstitial at a hexagonal site.³⁻⁵ We show that in Ge the $\langle 110 \rangle$ -split dumbbell configuration is also the lowest-energy configuration. However, we argue that in Ge there are four atoms in a bent, kitelike configuration, that have equivalent bonds in the defect, rather than two atoms as in the Si dumbbell. We also show conclusively that the (+/0) level cannot be positioned close to the bottom of the conduction band, and suggest that the observed level in the PAC experiments is the (0/-) level.

The present calculations follow exactly the same procedure used before in the study of the vacancy,⁸ namely *ab initio* total energy calculations based on the density-functional theory with the local-density approximation (LDA) for the exchange-correlation potential.⁹ We used a supercell with 128 atoms plus an extra one to describe the germanium interstitial. The electron-ion interactions were described using norm-conserving pseudopotentials of Bachelet, Hamann, and Schlüter¹⁰ in the Kleinman-Bylander¹¹ form. A plane-wave basis set was used with an energy cutoff of 12 Ry and the Brillouin zone was sampled using one \vec{k} point (Γ point). This size of supercell and number of \vec{k} -points used were shown to give reasonable results for the vacancy in our previous work.⁸ When performing geometry optimizations all the atoms were allowed to move until all components of the forces were smaller than 0.0005 hartree/bohr. For the calculations with the interstitial in the charge state q , a uniform charge density of $\rho = -q/\Omega_{cell}$ is added to the unit cell of volume Ω_{cell} to ensure that the whole system is charge neutral.

We have considered three configurations for the self-interstitial: (1) the $\langle 110 \rangle$ dumbbell; (2) a hexagonal site; and (3) a tetrahedral site. Among these, the lowest-energy configuration was found to be the $\langle 110 \rangle$ dumbbell, similarly to Si. It is 0.65 eV lower in energy than the hexagonal configuration and 0.90 eV lower than the tetrahedral one. These results show that the $\langle 110 \rangle$ dumbbell is significantly more stable in Ge than in Si, where Zhu *et al.*⁵ found that the $\langle 110 \rangle$ dumbbell is only 0.1 eV more stable than the hexagonal site. This difference may help to explain why the self-diffusion in Si has a contribution from interstitials whereas in Ge it is basically mediated by vacancies.^{4,12} In the following we present a detailed analysis only for the $\langle 110 \rangle$ dumbbell, since it is much more stable than all the other configurations.

The local atomic configuration around the $\langle 110 \rangle$ dumbbell is shown in Fig. 1. As can be seen, the distance between the two atoms forming the dumbbell is equal to 2.60 Å (D

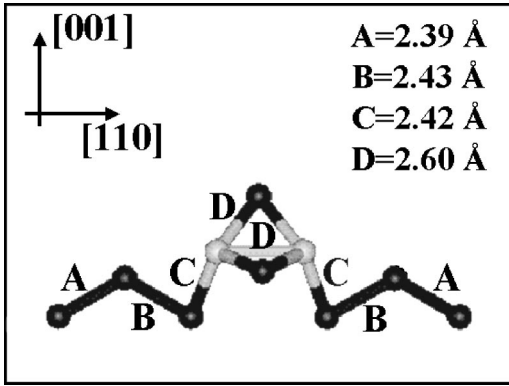


FIG. 1. Local geometry around the kite defect. The dumbbell atoms are shown lighter than the others. Note that all the five bonds shown in the kite have the same length equal to 2.60 Å (D bonds).

bond in Fig. 1), which is about 7.4% longer than the normal Ge-Ge bond length in the crystal (our theoretical value is 2.42 Å). This increase in the Ge-Ge distance, when compared to the nearest-neighbor distance in the crystal, is larger than the corresponding one obtained by Zhu *et al.*⁵ in Si, which is only about 3%. The two atoms forming the dumbbell move upwards by approximately 0.9 Å along the [001] direction, away from the original lattice site. Moreover, the four bond lengths between these two atoms and their two nearest-neighbor atoms in the (110) plane are all identical, and also identical to the Ge-Ge dumbbell bond length, i.e. there are a total of five identical bond lengths (the D bonds in Fig. 1). On the other hand, the two bond lengths between the dumbbell atoms and the two nearest-neighbor atoms in the ($\bar{1}10$) plane (C bonds in Fig. 1) are shorter than the D bonds, and have the same length as a normal Ge-Ge bond length in the crystal. Along the zigzag line in the (110) plane ([$\bar{1}10$] direction, not shown in Fig. 1), the distance between the nearest neighbors to the dumbbell atoms and their nearest neighbors is also identical to the normal Ge-Ge bond length in the crystal, i.e., 2.42 Å.

The bond lengths between the atoms in the zigzag line along the [110] direction (bonds A and B in Fig. 1) are very similar to the normal nearest-neighbor distance in the crystal, with variations of the order of 1%. However, similarly to Si, all these atoms along the [110] zigzag direction going through the dumbbell relax outward. We have obtained that for the first-neighbor atoms to the dumbbell, i.e., those connected to the dumbbell by bonds C in Fig. 1, the relaxations are about 0.07 Å, or 2.9% of the nearest-neighbor distance in the crystal. The relaxation is larger for the second-neighbor atoms to the dumbbell along the zigzag line, of the order of 0.13 Å, or 5.4% of the nearest-neighbor bond in the crystal. Finally, the third-neighbor atoms along the zigzag line relax by about 0.09 Å, or 3.7% of the nearest-neighbor distance in the crystal. Therefore, one can see that, even though all the bond lengths along the zigzag line in the [110] direction are close to their ideal values, the relaxations decay slowly.

The total charge densities along the ($\bar{1}10$) and (110) planes are shown in Figs. 2(a) and 2(b), respectively. Except between the two atoms forming the dumbbell, one can see the characteristic pattern of covalent bonds being formed be-

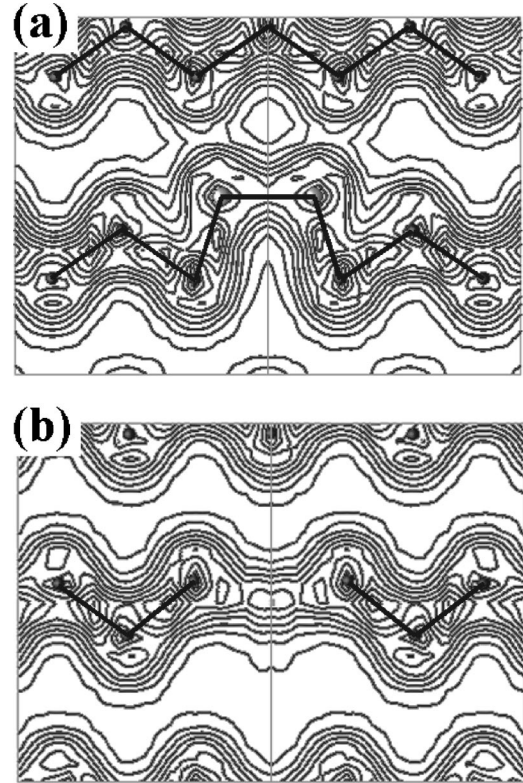


FIG. 2. Contour plots of the total charge densities on the (a) ($\bar{1}10$) and (b) (110) planes through the middle of the $\langle 110 \rangle$ dumbbell. The positions of the Ge atoms are indicated by the filled circles, and the dumbbell atoms are shown lighter than the others. The value of the most intense contour (middle of the bond between Ge atoms far away from the dumbbell) is $0.5 e/\text{Å}^3$, and the contours decrease in steps of $0.05 e/\text{Å}^3$.

tween all the other pairs of Ge-Ge atoms that are nearest neighbors. Analyzing a three-dimensional plot of the total charge density in the proximity of the interstitial defect, we actually obtain that it is somewhat delocalized around the four-atoms ring formed by the two Ge atoms in the dumbbell and their two nearest neighbors along the [$\bar{1}10$] direction, i.e., all the atoms separated by distance D in Fig. 1. Therefore, based both on the geometrical as well as total charge density analysis, it seems that the best description for the interstitial $\langle 110 \rangle$ dumbbell in Ge is not actually of a dumbbell, as in Si, but rather of a four-atoms ring strongly attached to the lattice, which we propose to name the “kite defect” ($\langle 110 \rangle$ -interstitial kite defect).

The formation energy of an interstitial in charge state q , $E_q^i(\mu_e)$, is calculated in the supercell approximation as

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

where E_q^{N+1} is the total energy of the supercell with an interstitial in charge state q ($N+1$ atoms),¹³ E^N is the total energy of the perfect lattice supercell (N atoms), μ_e is the position of the electronic chemical potential relative to the top of the valence band, E_v . The top of the valence band has been corrected in the defect supercells by the average potential around the furthest interstitial from the defect site.⁸ The formation energy results 2.29 eV for a neutral charge

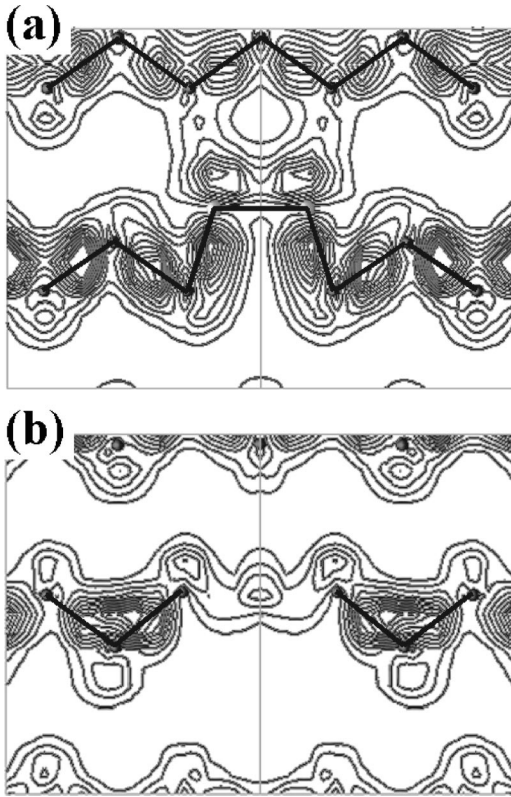


FIG. 3. Contour plots of the added charge densities for the three HOMO's on the (a) $(\bar{1}10)$ and (b) (110) planes through the middle of the $\langle 110 \rangle$ dumbbell. The positions of the Ge atoms are indicated by the filled circles, and the dumbbell atoms are shown lighter than the others. The value of the most intense contour (middle of the bond between Ge atoms far away from the dumbbell) is $0.01 e/\text{\AA}^3$, and the contours decrease in steps of $0.001 e/\text{\AA}^3$.

state, much smaller than for Si (3.2 eV).⁵ We also obtained (for $\mu_e = 0$ eV) 2.21 eV for the (+) charge state and 2.59 eV for the (−) charge state. Using the above equation we can obtain the ionization levels, i.e., the chemical potential values where the formation energies of two charge states become equal. Our results give for the (+/0) level a value of $E_v + 0.07$ eV and for the (0/−) level a value of $E_v + 0.31$ eV.

Using the PAC method, Haesslein *et al.*⁷ suggested the existence of a donor level close to the conduction band ($E_c - 0.04$ eV) for the interstitial, which they have assigned to the (+/0) level. Our result for the (+/0) level disagrees with this assignment. As mentioned above, we obtain that the (+/0) level is located at 0.07 eV above the top of the valence band, which is incompatible with the experimental result. In Figs. 3(a) and 3(b) we present the charge densities on the $(\bar{1}10)$ and (110) planes, respectively, obtained by adding the charge densities for the three highest occupied orbitals (HOMO's). We consider these three HOMO's together because they are basically degenerate. As can be seen, these orbitals are highly delocalized, with a large valence band character. Therefore, the (+/0) level, which involves these orbitals, must be located close to the top of the valence band, as we obtained, and not close to the bottom of the conduction band, as suggested by Haesslein *et al.*⁷ From the charge density in Fig. 3(a), it seems that these HOMO's are a mixture of a weak π bond between the two dumbbell Ge atoms strongly

coupled to the top of the valence band through a σ -like bond between the dumbbell atoms and their nearest neighbors along the $[110]$ zigzag line. As opposed to the HOMO's, an analysis of the lowest unoccupied orbital (LUMO) shows that it is highly localized around the defect. It has a clear π^* character, i.e., a π -anti-bonding orbital with a strong contribution coming from p orbitals centered on the two dumbbell atoms and oriented along the $[\bar{1}10]$ direction.

If the changes in the PAC signal are not related to the (+/0) dumbbell level, then we have the following possibilities: (1) The observed defect is not an interstitial. This is very unlikely in view of more recent experimental work.¹⁴ (2) The interstitial is not at the $\langle 110 \rangle$ configuration. This is also unlikely given the much greater stability of this configuration, as shown above. (3) Finally, a different $\langle 110 \rangle$ dumbbell ionization level is responsible for the changes in the PAC signal. This is the most likely explanation according to our results, and we argue below that the (0/−) level is the one related to the alterations in the PAC signal on the n -type Ge side.

According to the PAC results,⁷ the interstitial is trapped at the ^{111}In atoms in a broad range of doping concentrations, for both n - and p -type Ge. Therefore, there must be an attractive interaction between the Ge self-interstitials and the probe atoms over this large range of doping. The ^{111}In atoms are shallow acceptors, and therefore are negatively charged. As a consequence, to have an attractive interaction between the interstitial and the ^{111}In atoms, the interstitial charge state must be either (0) or (+), but not (−). The (0) charge state was discarded by the authors⁷ because, as the trapping to the ^{111}In atoms was effective for n -type Ge up to Sb concentrations of $5 \times 10^{17} \text{ cm}^{-3}$, there did not seem to be any good reason for the neutral interstitials to be so much more attracted to the negatively charged ^{111}In atoms instead of the positively charged Sb donors. Therefore, they were led to conclude that the interstitial was in the (+) charge state and that the attractive interaction between the ^{111}In atoms and the interstitials was Coulombic. Furthermore, assuming that the loss of the PAC signal on the n -type side was due to an interstitial charge change, the (+/0) level was assigned to be at 0.04 eV below the bottom of the conduction band.

However, our results, as discussed above, are incompatible with this conclusion. On the other hand, our (0/−) level is positioned at 0.12 eV below the bottom of the conduction band (for our theoretical gap⁸ of 0.43 eV), which is similar to the experimental result. We only need an attractive interaction between the ^{111}In atoms and the neutral interstitials. As a possible mechanism we propose that the neutral interstitials act as donors to the ^{111}In atoms, i.e., some of the ^{111}In atoms would become negatively charged not through an electron transfer from the valence band but rather from the neutral interstitials. In this way there would be the formation of a pair $\text{In}^- - \text{I}^+$, strongly attracted through the Coulomb interaction. We believe this to be possible due to the strong valence band character of the HOMO's, as shown above. Therefore, the disappearance of the PAC signal on the n -type side would be due to a change in the charge state of the interstitial from (0) to (−), which would result in a Coulomb attraction between the interstitial and the Sb^+ donors, as well as a repulsive interaction with the In^- probe atoms.

On the p -type side, the loss of the PAC signal can be interpreted by the influence of the competing Ga trapping centers, as already suggested by Haesslein *et al.*⁷ However, this competition may happen with the neutral as well as with the positively charged interstitial. Therefore, it may very well be that the decay of the PAC signal in the p -type side is related to the (+/0) level. If this is true, we estimate from the work of Haesslein *et al.*,⁷ using similar arguments as they

have used in that work, that the (+/0) level would be between 0.11 eV and 0.16 eV above the top of the valence band, in reasonable agreement with our result.

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- ¹G. D. Watkins, in *Defects and Their Structure in Non-metallic Solids*, edited by B. Henderson and A. E. Hughes (Plenum, New York, 1976), p. 203; G. D. Watkins and J. R. Troxell, *Phys. Rev. Lett.* **44**, 593 (1980); G. D. Watkins, in *Deep Centers in Semiconductors*, edited by S. T. Pantelides (Gordon and Breach, New York, 1986), p. 147.
- ²G. A. Baraff, E. O. Kane, and M. Schlüder, *Phys. Rev. Lett.* **43**, 956 (1979); *Phys. Rev. B* **21**, 5662 (1980).
- ³Y. Bar-Yam and J. D. Joannopoulos, *Phys. Rev. B* **30**, 2216 (1984).
- ⁴P. E. Blöchl, E. Smargiassi, R. Car, D. B. Laks, W. Andreoni, and S. T. Pantelides, *Phys. Rev. Lett.* **70**, 2435 (1993).
- ⁵J. Zhu, T. D. dela Rubia, L. H. Yang, C. Mailhot, and G. H. Gilmer, *Phys. Rev. B* **54**, 4741 (1996), and references therein.
- ⁶See *Germanium Silicon: Physics and Materials*, Vol. 56 of *Semiconductors and Semimetals* (Academic, San Diego, 1999).
- ⁷H. Haesslein, R. Sielemann, and C. Zistl, *Phys. Rev. Lett.* **80**, 2626 (1998); *Mater. Sci. Forum* **258-273**, 59 (1997).
- ⁸A. Fazzio, A. Janotti, A. J. R. da Silva, and R. Mota, *Phys. Rev. B* **61**, R2401 (2000); A. Janotti, R. Baierle, A. J. R. da Silva, R. Mota, and A. Fazzio, *Physica B* **273/274**, 575 (1999).
- ⁹M. Bockstedte, A. Kley, J. Neugebauer, and M. Scheffler, *Comput. Phys. Commun.* **107**, 187 (1997).
- ¹⁰G. B. Bachelet, D. R. Hamann, and M. Schlüter, *Phys. Rev. B* **26**, 4199 (1982).
- ¹¹L. Kleinman and D. M. Bylander, *Phys. Rev. Lett.* **48**, 1425 (1982).
- ¹²R. J. Borg and G. J. Dienes, *An Introduction to Solid State Diffusion* (Academic Press, San Diego, 1988); H. D. Fuchs, W. Walukiewicz, E. Haller, W. Dondl, R. Schorer, G. Abstreiter, A. I. Rudnev, A. V. Tikhomirov, and V. I. Ozhogin, *Phys. Rev. B* **51**, 16 817 (1995); A. Ural, P. B. Griffin, and J. D. Plummer, *Phys. Rev. Lett.* **83**, 3454 (1999).
- ¹³In the calculation of the total energies for the (+) and (−) charge states all the atoms were allowed to relax, having as starting configuration the optimized geometry from the (0) charge state. However, both the geometries (largest atomic motion was 0.017 Å) and total energies (changes smaller than 0.05 eV) changed very little upon relaxation.
- ¹⁴R. Sielemann, H. Haesslein, L. Wende, and Ch. Zistl, *Physica B* **273/274**, 565 (1999).