Lifetimes of positrons trapped at Si vacancies

Mineo Saito
NEC Informatec Systems, Ltd., 34, Miyukigaoka, Tsukuba 305, Japan

Atsushi Oshiyama*
Fundamental Research Laboratories, NEC Corporation, 34, Miyukigaoka, Tsukuba 305, Japan
(Received 14 November 1995)

We present first-principles calculations on positron lifetimes at various vacancies in Si. Lattice relaxation and electron redistribution caused by the vacancy *and* by the positron are included using the two-component density-functional theory. The calculated lifetimes are in agreement with the experimental data for the monovacancies and the divacancies and provide a new assignment of the longer lifetimes measured previously to stable multivacancies.

I. INTRODUCTION

Vacancies are fundamental defects in materials and have crucial effects on various properties of the host materials. The Si vacancy is a paradigm among them and has been studied due to its technological importance.[1,2] The vacancy of various sizes is created by electron or other particle irradiation on Si or by dry etching in modern semiconductor technology. The small vacancies, i.e., monovacancies and divacancies, induce deep levels in the fundamental gap and the levels are detected by, for instance, electron paramagnetic resonance (EPR) experiments.[1] Pioneering studies[3] have also found some EPR centers related to large vacancies (multivacancies) and assigned them to a pentavacancy (V_5), tetravacancies (V_4), and the trivacancy (V_3), respectively (Fig. 1). Yet a simple calculation based on the dangling-bond-counting model[4] has predicted that the hexavacancy (V_6) in the shape of a closed hexagon and the decavacancy V_{10} in the shape of an adamantine cage are stable. The stability of the multivacancy V_n with the particular value of n (magic number of multivacancies) has been supported by recent local-density-approximation (LDA) total-energy calculations:[2] The V_n with $n=4m+2$ ($=6, 10, 14, \ldots$) is actually found to be stable. Microscopic identification of the Si multivacancy has thus become an important issue in both science and technology.

Positron annihilation experiments have emerged as a promising tool to provide microscopic information on the vacancy-type defects.[5–7] A positron captured by the vacancy is mainly annihilated with a localized electron, leading to an increase of its lifetime compared with the free annihilation with an extended Bloch electron. The increase in the lifetime correlates positively with the vacant space inherent to each multivacancy. Positron annihilation experiments in the past indeed observed several lifetimes of the positron, depending on irradiation and annealing conditions: 270 ps,[5] 295–325 ps,[8] and longer lifetimes ranging from 320 to 500 ps,[9,10] all of which are longer than 218 ps (Ref. 5) observed in vacancy-free samples. The first two groups are assigned to the monovacancy (270 ps) and to the divacancy (295–325 ps), respectively, based on some calculations[7,11–14] and on empirical experiences. Yet the assignment of the longer lifetimes is still full of ambiguity. Although a calculation[12] of the lifetimes for multivacancies has been performed, the method is rather crude: The electron density is simply assumed to be a superposition of free-atom densities (SFAD) and geometry optimization is not carried out. Self-consistent calculations are imperative to obtain quantitative values of the lifetimes for the Si vacancies.

In this study, first-principles calculations on positron lifetime are performed based on the two-component density-functional theory for electrons and positrons with the LDA for exchange-correlation energy.[6] A supercell (repeating large unit cell geometry) approximation[7] is used to simulate a defect accompanied with lattice relaxation in an otherwise perfect crystal. The present self-consistent calculations include both electronic and ionic relaxations induced by the positron. Recent calculations[15] for the positron annihilation at As vacancy in GaAs, which use a similar method to ours, have successfully obtained the positron lifetime. We find here that our calculations provide reliable lifetimes of the positron trapped at monovacancies, divacancies, and multivacancies and hereby offer a firm theoretical framework to study the Si vacancies through the positron annihilation experiments: Inclusion of atomic relaxation induced by the positron is essential to reproduce the experimental lifetimes at monovacancies and divacancies; the calculated lifetimes for multivacancies up to V_{10} are generally shorter than those postulated in the past; a new interpretation on the experimental lifetimes at the multivacancies is then proposed.

II. METHOD

Boroński and Nieminen[16] (BN) have proposed two calculational schemes of the two-component density-functional theory within the LDA: In one scheme, the electron-positron correlation energy is calculated within the approximation based on the zero-positron-density limit, whereas in the other one it is done within the approximation based on the equal densities of electrons and positrons. We choose the zero-positron-density limit, following Gilgien *et al.*[15] who have obtained successful results for the As vacancy in GaAs. The electron-positron correlation energy in the above limit is the energy gained when a single positron is put in a homoge-

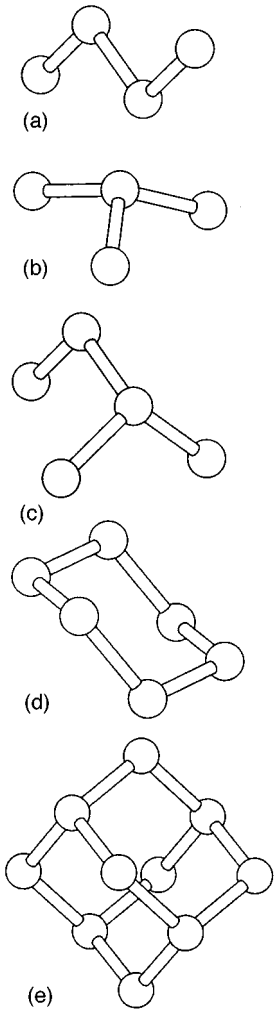

FIG. 1. Configuration of vacant sites in multivacancies: V_4 with a zigzag chain (a) and a trigonal pyramid (b), V_5 with a nonplanar shape (c), V_6 with a closed hexagon (d), and V_{10} with an adamantine cage (e).

neous electron gas. This energy is calculated by Arponen and Pajanne[17] and is interpolated by BN.[16] As for the electron-electron exchange correlation energy, we use the results calculated for the homogeneous electron gas model by Ceperley and Alder.[18] We employ the norm-conserving[19] pseudopotential for valence electrons and a local pseudopotential[20] for a positron to simulate the ion cores, the 64-site supercell, one k point for the Brillouin zone integration, and the 16-Ry cutoff energy for the plane-wave basis set. In the geometry optimization, we *fully* relaxed atoms, i.e., all the atoms in the supercell are relaxed in order to take the medium range of relaxation. The force acting on each atom is less than 0.001 Ry/a.u. in the optimized geometry as in previous studies on Si vacancies without positrons.[2,21,22] Minimization of the total energy over the degrees of freedom in positron and valence electron densities and atomic positions is performed using the conjugate-gradient technique, which is one of the iterative minimization techniques[23] initiated by Car and Parrinello.[24] Details of application of the conjugate-gradient technique to the study of Si vacancies were reported previously.[2,21,22] After the electron and positron densities are determined for the optimized geometry, we evaluate the rate of positron annihilation with valence electrons:

$$\lambda_{\mathrm{val}} = \pi r_0^2 c \int dr\, \rho_{\mathrm{val}}(r)\rho_p(r)g_0(\rho_{\mathrm{val}}). \tag{1}$$

Here, r_0 is the classical electron radius, c the speed of light, ρ_{val} and ρ_p are valence electron and positron densities, respectively. The enhancement factor $g_0(\rho_{\mathrm{val}})(>1)$ originating from the correlation for electron-positron attractive interaction is deduced from the value of the pair distribution function at the origin for the case of one positron in a homogeneous electron gas. BN have provided this enhancement factor based on Lantto's hypernetted chain approximation calculation.[25] The rate of the core electron annihilation (λ_{core}) gives minor contribution to the positron lifetime ($1/\tau = \lambda_{\mathrm{val}} + \lambda_{\mathrm{core}}$) in the case of Si. We evaluate this rate by using the frozen core electron density obtained from the free-atom calculation within the LDA and the enhancement factor, which is the same as in (1). In the calculation for Si vacancies, the neutral charge state is assumed for the vacancies because of rather high temperatures in experimental situations. For some vacancies with high symmetry, we have clarified that Jahn-Teller (symmetry-lowering) distortions[1] occur. Yet we have found from 10-Ry cutoff energy calculations that the lifetimes vary by only 1–2 ps due to the Jahn-Teller effect for V and V_2.[26] We thus neglect the effect in the present calculations.

The used parameters (cell size, cutoff energy for the plane-wave basis set, and sampling k points) have been examined in previous studies on monovacancis and divacancies without positrons.[21,22] We further examine the accuracy of the present calculation on vacancies capturing positrons. We first check whether the used cutoff energy provides the converged positron lifetime for a given geometry of vacancies. The monovacancy is chosen in this examination since the wave function in this vacancy is the most localized among the Si vacancies. The lifetime calculated with the 12-Ry cutoff energy agrees within 1 ps with those in the cases of the 16- and 20-Ry cutoff energies, indicating that the 16-Ry cutoff energy, which is used throughout the present calculations, gives the converged value. Next we examine whether the cutoff energy is sufficient to obtain a reliable optimized geometry. The calculated displacement of the nearest atoms in the case of 12 Ry is found to deviate by 0.06 Å compared with that in the case of 16 Ry. However, the latter value deviates by only 0.02 Å from that in the case of 20 Ry. This small deviation in the displacement corresponds to that of 2 ps in the positron lifetime. The present *full* geometry optimization displaces the boundary atoms in the unit cell by less than 0.05 Å for the vacancies up to hexavacancy. The supercell approximation in this study is thus expected to be sufficient to describe atomic relaxation for the vacancies. Yet the present supercell is slightly insufficient for describing decavacancy (Fig. 1): the largest distance between the vacant sites (two sites are on a [100] line) is half of the lattice length of the present cubic cell of 64 sites. The present enhancement factor based on the homogeneous electron gas model does not include the *imperfect* screening due to finite band gap in semiconductors. Yet, since the calculated lifetime (215 ps) for the bulk (the positron is in its lowest Bloch state) is close to the experimental value [218 ps (Ref. 5)], we apply

the above-mentioned enhancement factor to the Si case. The same enhancement factor was applied to the GaAs system by Gilgien *et al.*[15] Puska proposed a *reduced* enhancement factor that includes the finite gap effect.[27] The linear-muffin-tin-orbital (LMTO) atomic-sphere-approximation (ASA) calculation with this enhancement factor gives the lifetime of 221 ps for the bulk, which is only slightly longer than the present value.

III. RESULTS AND DISCUSSION

At monovacancy (V), the calculated wave function of the positron in the ground state is found to have the maximum amplitude at the vacancy site. One of the important results is that this vacancy is accompanied with large atomic relaxation due to capture of the positron. In the optimized geometry, we find that the nearest-neighbor Si atoms are displaced outwards (away from the vacancy site) by 0.24 Å and the angle (θ) of the nearest atom back bonds thus becomes larger (114.4°) than the tetrahedral angle (109.5°) of the ideal vacancy without relaxation. This prominent outward displacement is in sharp contrast with the previously reported inward displacement when the positron is not captured.[21] The inward displacement of the vacancy without the positron is due to the energy gain by the s-p hybridization in the dangling bond: the decrease of θ from the tetrahedral angle increases the s component in the dangling bond and lowers the total energy.[28] On the other hand, the outward displacement in the case of positron capturing increases the energy with less s component in the dangling bond but decreases the energy by reducing Coulomb repulsion between the positron and nearest ion cores: since the positron wave function has the maximum amplitude at the vacancy site, the outward displacement prolongs the distance from the maximum point to the nearest atoms. It is emphasized that this outward displacement of the nearest atoms considerably prolongs the lifetime, since the overlap between the electron and positron densities becomes small. Actually the calculated lifetime (279 ps) for the relaxed geometry is much longer than that (256 ps) for the ideal vacancy. The value for the relaxed case is in good agreement with the experimental value (270 ps).[5]

At divacancy (V_2), we find that the maximum amplitude of the positron wave function is located in the middle of the two vacant sites (Fig. 2). The six nearest-neighbor atoms are found to be displaced outwards in contrast with the previously reported inward displacement in the divacancy without the positron.[22] This outward displacement induced by positron capturing is similar to that in the monovacancy case but is relatively small. The displacement is 0.09 Å [$\theta=111.9°$ (Ref. 29)]. As a result, the lattice relaxation effect in V_2 prolongs the lifetime by 11 ps, which is small compared with the value of 23 ps in V. Experimental lifetimes for V_2 reported by several groups[8] are in the range of 295–325 ps. The lifetime from the present calculation is 309 ps, which agrees with the experimental values.

The present method reproduces experimental positron lifetimes for bulk, V, and V_2 (Table I). This manifests its capability of predicting the lifetimes for large vacancies from trivacancy (V_3) to decavacancy (V_{10}). The calculated lifetime (320 ps) for V_3 is longer by only 3 ps than that of the ideal trivacancy, indicating that the lattice relaxation effect on the positron lifetime is small compared with the cases of V and V_2. As for the eight threefold-coordinated atoms around V_3, the two atoms along the zigzag chain of the vacancy sites are displaced outwards by 0.14 Å ($\theta=112.8°$) while the other six atoms are displaced by only 0.02–0.06 Å. Plural configurations of the vacant sites exist when the multivacancy is larger than V_3. We here choose a zigzag chain and a nonplanar configurations for V_4 and V_5 (Fig. 1), respectively. (These configurations are assigned to the EPR centers labeled as $P3$ and $P1$, respectively in early experiments.[3]) The calculated lifetimes for the V_4 (325 ps) and the V_5 (345 ps) are found to be very close to those (326 and 347 ps, respectively) for the unrelaxed counterparts. Indeed the displacement of threefold-coordinated atoms is small (0.05–0.06 Å in V_4 and 0.06–0.14 Å for V_5). We also study V_4 with a trigonal pyramid (Fig. 1), which is assigned to the EPR center $A3$ in the past.[3] The calculated lifetime for relaxed (ideal) geometry is 337 (338) ps. This value is longer by 12 ps than that with the zigzag chain. We next study two defects that are expected to be particularly stable in samples from previous total-energy calculations,[2,4] i.e., V_6 and V_{10} (Fig. 1). In our optimized geometry of V_6, the nearest atoms of the two types are displaced inwards by 0.22 and 0.20 Å ($\theta=108.0°$ and 106.1°). This inward displacement, in contrast with the outward displacement in V and V_2, prominently *reduces* the lifetime (348 ps) by 13 ps. As was mentioned in Sec. II, the present cell size is slightly insufficient to describe V_{10} (Fig. 1). We, however, tentatively perform calculations for this large vacancy. The calculated lifetime of the ideal vacancy is 394 ps and that for the relaxed vacancy is 386 ps.

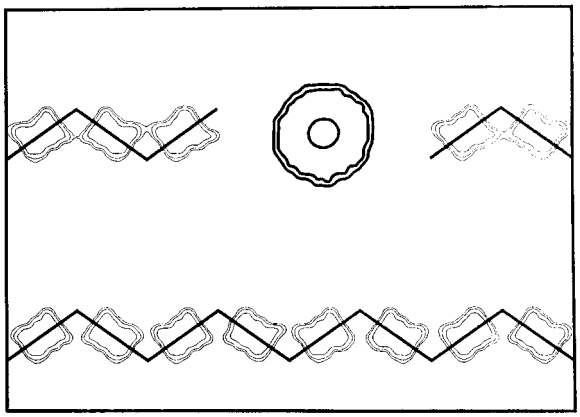

FIG. 2. Positron and electron densities in V_2 on the $(1\bar{1}0)$ plane. The former [latter] densities are represented by thick [thin] lines and their values are 0.02, 0.01, and $0.005e$/(a.u.)^3 [-2.0, -1.0, and $-0.5e$/(a.u.)^3].

Figure 3 summarizes the lattice relaxation effect on the lifetimes for vacancies. In small vacancies (V and V_2), the positron capturing enlarges the open volume of the defects by displacing the nearest atoms outwards and thus prolongs the lifetimes. As the vacancy becomes large, the above increase of the volume due to the positron capturing is suppressed. Thus, in the large vacancy of V_6, the open volume is decreased by the inward displacement of the nearest at-

TABLE I. Positron lifetimes in Si. λ_{core} and λ represent annihilation rates for the core and total electron charges, respectively.

	Theory (ps)	$\lambda_{core}/\lambda \times 100$	Expt. (ps)
Bulk	215	2.37	218 (Ref. 5)
V	279	0.67	270 (Ref. 5)
V_2	309	0.50	295–325 (Ref. 8)
V_3	320	0.48	
V_4 (zigzag chain)	325	0.46	
V_4 (trigonal pyramid)	337	0.43	
V_5	345	0.41	
V_6	348	0.45	
V_{10}	386 [a]	0.29	

[a]The present cell size is slightly insufficient to describe V_{10} (see text).

oms. (This inward displacement originates from the stabilization of the dangling bonds of the nearest atoms as mentioned above.) As a result, the lifetime becomes short compared with the value of the unrelaxed counterpart. As shown in Table I, the contribution of the core electron annihilation to the total annihilation rate is very small and tends to decrease as the size of the vacancy becomes large.

Finally, the present lifetimes are compared with those of previous studies. The positron states in ideal Si vacancies were calculated using the electron density obtained in the self-consistent manner for the systems without positrons[11,14] or the SFAD,[12–14] i.e., all these calculations are based on the assumption that the electron density is not affected by the localized positron. The used enhancement factors in these calculations are slightly *reduced* compared with the present one. The LMTO-ASA Green's-function method[11] gives the lifetime of 249–259 ps (Refs. 11 and 14) for V and the simplified SFAD method provides similar values of 250–256 ps.[12–14] As for V_2, the SFAD method gives the lifetime of 306–309 ps.[12,13] These reported values are comparable with the present values for the unrelaxed case (256 ps for V and 298 ps for V_2). It is noted, however, that the present lifetimes for large vacancies are shorter than the values previously reported by Puska and Corbel[12] based on the SFAD method (Fig. 3). The lifetime by Puska and Corbel for V_4 is 354 ps, much larger than the present values (326 and 338 ps) for the above-mentioned two configurations without lattice relaxation.[30]

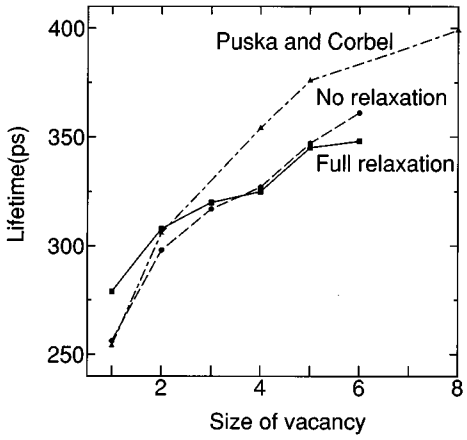

FIG. 3. The lifetime of the positron captured at the vacancy of each size. The solid and dashed lines indicate lifetimes for the relaxed and ideal geometries, respectively. The results in a previous calculation by Puska and Corbel (Ref. 12) are also plotted. As for V_4, we plot the value of our calculation for the zigzag chain configuration.

Kawasuso *et al.* find a peculiar defect characterized by the positron lifetime of 320 ps with the maximum concentration for the annealing at 175 °C.[10] Although the lifetime of 320 ps is usually attributed to V_2,[5] infrared light absorption measurement indicates that the defect is different from V_2. The present calculation provides a successful interpretation on this embarrassing experimental result: the defect observed by Kawasuso *et al.* is likely to be V_3 or V_4 having the zigzag chain. (The calculated lifetimes are 320 ps and 325 ps, respectively.) Kawasuso *et al.* also find the lifetimes of 350 and 400 ps at higher temperatures and assign them to those of V_4 and V_6, respectively. Yet, since the lifetime of 350 ps is close to calculated values of V_5 (345 ps) and V_6 (348 ps), the lifetime is expected to be due to V_5 or V_6. We speculate that the measured lifetime of 400 ps is due to a vacancy that is larger than V_6. V_{10} with the calculated lifetime of 386 ps is a candidate for this vacancy. In earlier experimental works, the measured lifetime of 435 ± 30 ps is attributed to V_4.[9] Present results suggest, however, that the detected vacancy is much larger than V_6.

IV. SUMMARY

We have calculated lifetimes of a positron captured at various Si vacancies, based on the two-component density-functional theory with the LDA, and clarified the importance of the lattice relaxation to obtain reliable lifetimes. While the increase of the open volumes in small vacancies (V and V_2) prolongs the lifetimes, the decrease of the volume in a large vacancy (V_6) shortens the lifetime. We confirm that the present method successfully reproduces the experimental lifetimes for bulk, monovacancies, and divacancies. For large vacancies up to V_{10}, the calculated lifetimes for each V_n is generally shorter than those obtained from the previous theoretical study.[12] We have then examined the assignments of measured lifetimes in the past and proposed a new assignment.

*Present address: Institute of Physics, University of Tsukuba, Tsukuba 305, Tsukuba, Japan.
[1] G. D. Watkins, in *Deep Centers in Semiconductors*, edited by S. T. Pantelides (Gordon and Breach, New York, 1986), p. 147.
[2] A. Oshiyama, M. Saito, and O. Sugino, Appl. Surf. Sci. **85**, 239 (1995).
[3] Y-H. Lee and J. W. Corbett, Phys. Rev. B **8**, 2810 (1973); **9**, 4351 (1974), and references therein.
[4] D. J. Chadi and K. J. Chang, Phys. Rev. B **38**, 1523 (1988).
[5] For a review, see S. Dannefaer, in *Proceedings of Defect Control in Semiconductors*, edited by K. Sumino (North-Holland, Amsterdam 1989), p. 1561.
[6] M. J. Puska and R. M. Nieminen, Rev. Mod. Phys. **66**, 841 (1994).
[7] M. Saito, A. Oshiyama, and S. Tanigawa, Phys. Rev. B **44**, 10 601 (1991).
[8] W. Fuhs, V. Holzhauer, S. Mantl, F. W. Richter, and R. Sturm, Phys. Status Solidi B **89**, 69 (1978); P. Mascher, S. Dannefaer, and D. Kerr, Phys. Rev. B **40**, 11 764 (1989); M. Kwete, D. Segers, M. Dorikens, L. D.-Vanpraet, P. Clauws, and I. Lemahieu, Appl. Phys. A **49**, 659 (1989); A. Kawasuso, M. Hasegawa, M. Suezawa, S. Yamaguchi, and K. Sumino, J. Jpn. Appl. Phys. **34**, 2197 (1995).
[9] S. Dannefaer, G. W. Dean, D. P. Kerr, and B. G. Hogg, Phys. Rev. B **14**, 2709 (1976).
[10] A. Kawasuso, M. Hasegawa, M. Suezawa, S. Yamaguchi, and K. Sumino, Mater. Sci. Forum **175-178**, 423 (1995).
[11] M. J. Puska, O. Jepsen, O. Gunnarsson, and R. M. Nieminen, Phys. Rev. B **34**, 2695 (1986).
[12] M. J. Puska and C. Corbel, Phys. Rev. B **38**, 9874 (1988).
[13] M. J. Puska, S. Mäkinen, M. Manninen, and R. M. Nieminen, Phys. Rev. B **39**, 7666 (1989).
[14] M. J. Puska, Mater. Sci. Forum, **105-110**, 419 (1992).
[15] L. Gilgien, G. Galli, F. Gygi, and R. Car, Phys. Rev. Lett. **72**, 3214 (1994).
[16] E. Boroński and R. M. Nieminen, Phys. Rev. B **34**, 3820 (1986).
[17] J. Arponen and E. Pajanne, Ann. Phys. (N.Y.) **121**, 343 (1979).
[18] D. M. Ceperley and B. L. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[19] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).
[20] The local potential has the form of $Z_v/r\mathrm{erf}(r/r_c)$ for positron's equation, where erf is the error function. In the above equation, Z_v is the ion core charge and r_c is taken to be 0.5 a.u. When this potential is replaced by the potential from the frozen core and nuclear point charges, the calculated lifetime for the bulk varies by only 2.5 ps.
[21] O. Sugino and A. Oshiyama, Phys. Rev. Lett. **68**, 1858 (1992).
[22] M. Saito and A. Oshiyama, Phys. Rev. Lett. **73**, 866 (1994); **74**, 4354 (1995).
[23] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).
[24] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
[25] L. J. Lantto, Phys. Rev. B **36**, 5160 (1987).
[26] The lifetime calculated with 10 Ry cutoff energy deviates by at most 8 ps compared with the case of 16 Ry.
[27] M. J. Puska, J. Phys. Condens. Matter **3**, 3455 (1991).
[28] M. Saito and A. Oshiyama, Mod. Phys. Lett. B **7**, 1567 (1993).
[29] Since the three angles among back bonds are different, we take the averaged value for θ.
[30] Figure 3 compares lifetimes of V_5 in Ref. 12 and in the present study. The configurations of the vacant sites in the two studies are, however, different from each other.