

# Investigation and calculation of positron lifetimes of mono-vacancies in crystals

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**Abstract.** The first-principles calculations of positron lifetimes of mono-vacancies in crystals were investigated. We use the two-component density functional theory to respectively compute positron lifetimes of neutral charge state of  $V_{Al}$  defect in aluminium,  $V_{Si}$  defect in silicon,  $V_C$ ,  $V_{Si}$  and  $V_C+CSi$  defects in 3C silicon carbide,  $V_{Ga}$  and  $V_{As}$  defects in gallium arsenide, taking into account atomic relaxation due to vacancy and electronic structural relaxation due to the presence of the positron. Three different calculation schemes are used. We find that the electron density inside the vacancy more or less increases due to the presence of the positron if the ionic positions are kept fixed, and the positron becomes more localized after the electronic structural relaxation for the case of  $V_{Al}$  defect in aluminium and  $V_{Si}$  defect in 3C silicon carbide, but it is opposite for the case of  $V_{Ga}$  defect in gallium arsenide and  $V_C$  defect in 3C silicon carbide. The results with no consideration of the relaxation are even much closer to the experimental ones, therefore the atomic relaxation due to the position play an important role in calculating the positron lifetime of mono-vacancies in crystals.

## 1. Introduction

As is well known, positron annihilation spectroscopy (PAS) has been a powerful nondestructive technique to probe open volume defect in materials. As a positron gets trapped in a vacancy-type defect, the positron lifetime increases and this can be measured by the positron lifetime spectroscopy. Moreover the vacancy-type defect often has a very close relationship to materials' property, so it is required to identify the type of defects corresponding to a specific lifetime comparison with other characterization methods or calculated lifetimes. The interpretation of the positron lifetime spectroscopy experimental results is usually based on theoretical lifetime calculations, especially the bulk lifetime calculations.

Positron lifetime in perfect crystals has been demonstrated successfully by first principles calculation in past decades. They all almost obtain the similar results in the conventional way and the self-consistent way. While for the situation of positron in mono-vacancies of materials, there still exist some disputes. It has been reached that positron can be easily trapped and entirely located by negative or neutral vacancies, but different calculating results of positron lifetimes of vacancies are obtained by different authors. The discrepancies among those controversial results are mainly caused by neglecting the change of electron density and potential, which is usually related to atomic relaxation induced by vacancies and the trapped positron. Moreover, different methods applied in the calculation process are



also lead to such discrepancies for positron lifetimes, such as superposed neutral atom model, pseudo-potential model, full-potential model, the local density approximation (LDA), the generalized gradient approximation (GGA), etc. Generally, in the conventional calculation scheme, the influence of the change of electron density and potential due to the presence of vacancies and positron was not taken into account, while these results agree with experimental ones much better than those results that all are considered in some situations, and this is the biggest dispute.

For the theoretical model, the electron pileup in the vacancy region due to the atomic relaxation induced by vacancies. Meanwhile, the presence of positron further attracts the electron around the vacancy region and repel atomic nucleus away from their balance position in the perfect crystal lattice, moreover, in the vacancy the positron density is not zero in fact and this diminishes contact rate, thus cancellation exists. Therefore further calculations and analysis need to be done carefully. Only a few of articles concerned about the fully-self-consistent scheme [1-4, 6]. Nieminen and Boronski et al [1,2] first proposed the two-component functional theory and applied it to calculate the positron lifetime of  $V_{Al}$  defect in aluminum, they found that the positron potential inside the vacancy became lower in self-consistent way than that in conventional way, and the positron distribution became more spread out. Puska et al [3] presented a self-consistent way to calculate the case of the ideal triply negative Ga vacancy in GaAs, the electron density inside the vacancy increased, and the positron became more localized as the trapped potential became lower. Julia Wiktor et al [4] used the pseudo-potential method to deal with the valence electrons, while the result they got was a little big different from the others, especially for the positron lifetime of  $V_C$  defect in SiC.

We present first-principle calculations of positron lifetimes in the vacancies in two schemes, one is the conventional way based on the one component density functional theory, and another is the self-consistent way based on the two component density functional theory. In the self-consistent way, we consider the influence induced by atomic relaxation due to the vacancy and the electronic structural relaxation due to the presence of the positron. In this paper, we choose Al, Si, GaAs and 3C-SiC as examples to calculate their corresponding mono-vacancy positron lifetimes, compare our results with the experiment lifetimes from the literatures.

## 2. Method

Theoretically, the positron annihilation rate  $\lambda$  takes the form related to the positron density  $n_+(\vec{r})$ , the electron density  $n_-(\vec{r})$  and the enhancement factor  $g_{12}(0; n_+(\vec{r}); n_-(\vec{r}))$ , and the positron lifetime  $\tau$  is just the inverse of the positron annihilation rate:

$$\frac{1}{\tau} = \lambda = \pi r_0^2 c \int d\vec{r} n_+(\vec{r}) n_-(\vec{r}) g_{12}(0; n_+(\vec{r}); n_-(\vec{r})), \quad (1)$$

where  $c$  is the speed of the light and  $r_0$  is the classical radius of an electron.

The electron and positron density can be calculated using various approximations, which leads to several schemes. In this study, we considered two schemes. One is the self-consistent way (SC) based on the two-component density-functional theory:

$$\begin{cases} -\frac{1}{2} \nabla^2 \psi_i(\vec{r}) + \left[ \frac{\delta E_{xc}[n_-]}{\delta n_-(\vec{r})} - \phi(\vec{r}) + \frac{\delta E_{corr}[n_+, n_-]}{\delta n_-(\vec{r})} \right] \psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r}); \\ -\frac{1}{2} \nabla^2 \psi_+(\vec{r}) + \left[ \frac{\delta E_{xc}[n_+]}{\delta n_+(\vec{r})} + \phi(\vec{r}) + \frac{\delta E_{corr}[n_+, n_-]}{\delta n_+(\vec{r})} \right] \psi_+(\vec{r}) = \varepsilon_+ \psi_+(\vec{r}). \end{cases} \quad (2)$$

$$n_-(\vec{r}) = \sum_i |\psi_i(\vec{r})|^2, n_+(\vec{r}) = |\psi_+(\vec{r})|^2, \quad \phi(\vec{r}) = \int d\vec{r}' \frac{-n_-(\vec{r}') + n_+(\vec{r}') + n_0(\vec{r}')}{|\vec{r} - \vec{r}'|}. \quad (3)$$

Where  $\psi_i(\vec{r})$  and  $\varepsilon_i$ ,  $\psi_+(\vec{r})$  and  $\varepsilon_+$  are respectively the electron wave function and its energy eigenvalue, the positron wave function and its energy eigenvalue,  $\frac{\delta E_{xc}[\mathbf{n}]}{\delta n(\vec{r})}$  is the electron or positron

exchange-correlation potential,  $\frac{\delta E_{corr}[\mathbf{n}_+, \mathbf{n}_-]}{\delta n(\vec{r})}$  is the electron or positron correlation potential, and

$n_0(\vec{r})$  denotes the density of positive charge providing the external potential. In this scheme, the presence of the positron influence the distribution of the electrons and ions, conversely the change of the electronic structure influence the distribution of the positron, the ground electron density and the positron density are determined through the self-consistent solution of equations (2) and (3). In our situation, there is only one positron in the solid at a time, if we assume that the electron density isn't affected by the presence of the positron at all, we can obtain the density from the one-component density-functional functions:

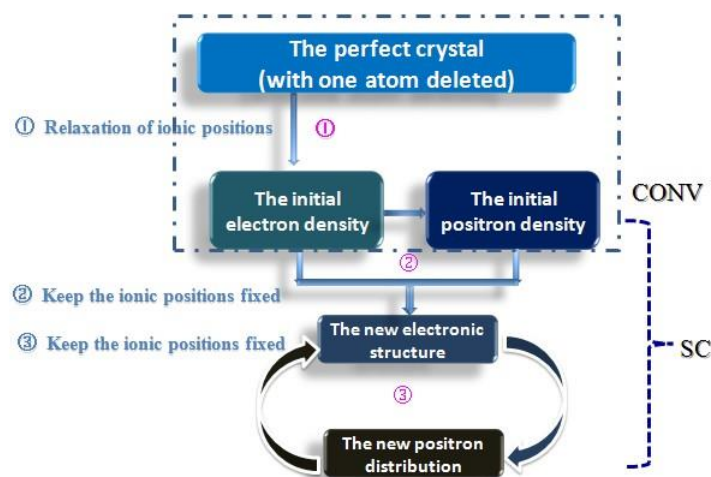
$$\begin{cases} -\frac{1}{2}\nabla^2\psi_i(\vec{r}) + [-\phi(\vec{r}) + \frac{\delta E_{xc}[\mathbf{n}_-]}{\delta n_-(\vec{r})}]\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r}); \\ -\frac{1}{2}\nabla^2\psi_+(\vec{r}) + [\phi(\vec{r}) + \frac{\delta E_{corr}[\mathbf{n}_+, \mathbf{n}_-]}{\delta n_+(\vec{r})}]\psi_+(\vec{r}) = \varepsilon_+\psi_+(\vec{r}). \end{cases} \quad (4)$$

$$\phi(\vec{r}) = \int d\vec{r}' \frac{-n_-(\vec{r}') + n_0(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad (5)$$

The electron density first, then the positron density, this is the so-called conventional way (CONV).

And for the enhancement factor which taking into account an increase in the electron density at the positron site caused by the screening of the positron by electrons, it is a crucial ingredient in the context of calculating the positron lifetimes in solids, there are many different parameterized forms so far. In this study, we chose three forms, one is proposed by Boronski and Nieminen (BNLDA) [2], the second one is proposed by Barbiellini and others (APGGA) [5], and the last one is parameterized by Puska, Seitsonen and Nieminen (PSN) based on the result of Boronski and Nieminen [6].

### 3. Computational details and testing



**Figure 1.** The schematic diagram of computational details.

We present a scheme as shown in figure 1 to calculate the positron lifetime for perfect crystals and crystals with vacancy-type defect. In the first step, we take a relaxation of ionic positions only due to the vacancy, then get the electron density as its initial values, then achieve the positron density by

solving the positron part of one-component density-functional equations as its initial values. In the second step, we keep the ionic positions fixed and relax the electronic structure due to the presence of the positron, then solve the two-component density-functional equation to get the new positron distribution. At last, repeat the second step until convergence is reached. In the CONV scheme, only the first step is needed.

Positron lifetime calculation is performed using the Vienna Ab-initio Simulation Package (VASP) [7, 8]. For the relaxation in the first step, we use a conjugate-gradient algorithm. The force acting on each ion is less than 0.001eV/Å. For the electronic structure, we adopt the PAW-PBE pseudo-potential [9] and plane wave basis set, and only take into account the valence electrons. The electron-electron exchange-correlation potential is performed using PBE-GGA method. And for the positron density, we use a real space grid method, the energy convergence is  $1.0e^{-7} a.u.$ .

For testing our program, we take the perfect crystals of Al, 3C-SiC, GaAs and Si as examples to calculate their bulk positron lifetimes. We use the experimental lattice parameters of 4.05 Å for Al, 4.33 Å for 3C-SiC and 5.43 Å for Si and theoretical lattice parameter of 5.57 Å for GaAs [3]. We take  $2s^2 2p^2$ ,  $3s^2 3p^1$ ,  $3s^2 3p^2$ ,  $4s^2 4p^1$  and  $4s^2 4p^3$  as valence electrons for C, Al, Si, Ga and As respectively. The results are presented in Table 1.

**Table 1.** Comparison of the bulk positron lifetime (in ps) calculated in CONV and SC way. Different forms of the enhancement factor (BNLDA, APGGA and PSN) were used. The corresponding experimental values are obtained from the literatures.

Crystal	BNLDA		APGGA		PSN		Exp.
	CONV	SC	CONV	SC	CONV	SC	
Al	186	184	164	162	197	194	161 <sup>a</sup>
3C-SiC	147	145	146	141	146	144	140 <sup>b</sup>
GaAs	242	230	246	234	253	249	231 <sup>c</sup>
Si	230	227	229	217	239	234	219 <sup>a</sup>

<sup>a</sup> Corresponding experimental results within reference 10.

<sup>b</sup> Corresponding experimental results within reference 11.

<sup>c</sup> Corresponding experimental results within reference 6.

It can be noticed in Table 1 that the bulk positron lifetimes calculated in CONV way are similar to that calculated in SC way for these four perfect crystals, which is consistent with the previous studies. Of course, as we only take into account of the valence electrons, neglect the annihilation rate of the core electrons, the bulk lifetimes are almost larger than the experimental ones especially for the case of aluminium which is metal. The results especially in APGGA/SC scheme are close to the experimental values. This means that our program is reliable. In PSN scheme, since the enhancement factor is parameterized based on another different positron-electron correlation potential [6], in this work we just deal with the positron-electron correlation potential in APGGA scheme, the results are a little different from the experimental ones, and this shows that the positron-electron correlation potential plays an important role in calculating the positron lifetimes.

#### 4. Results and discussion

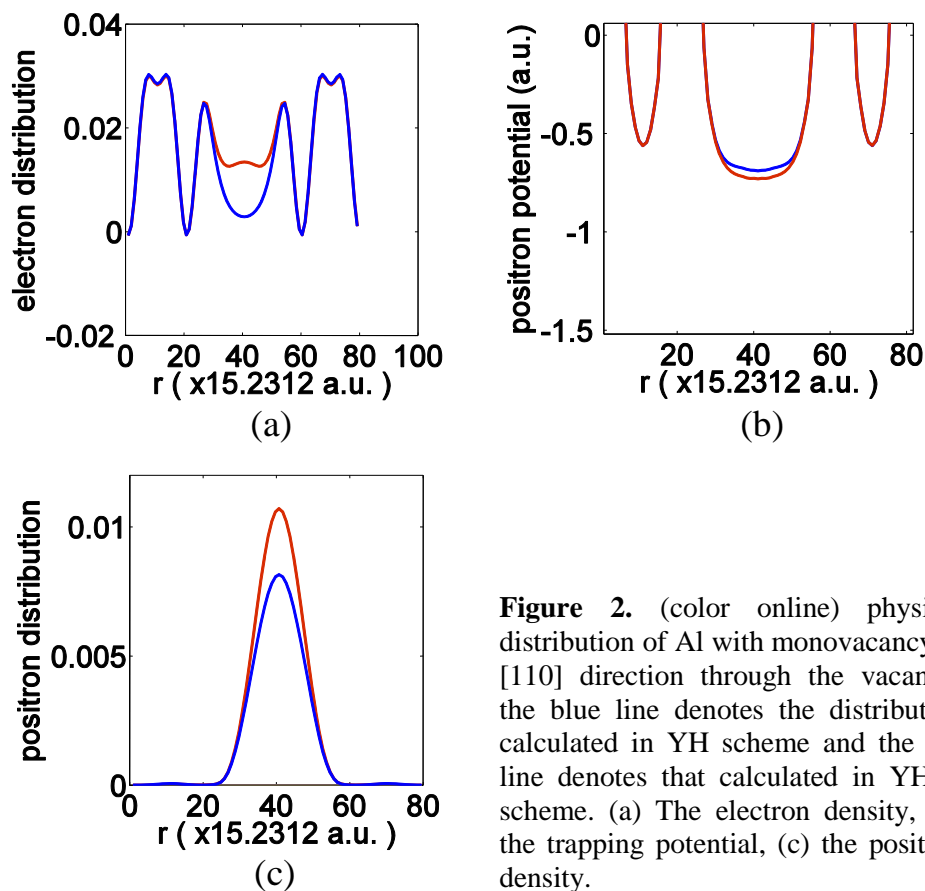
For mono-vacancies in crystals, we select three schemes, NYH stands for no relaxation due to the vacancy and the presence of the positron, YH stands for only relaxation of the ionic positions due to the vacancy and YH+P stands for the relaxation of the ionic positions firstly, then the relaxation of the electronic structure due to the presence of the positron. Otherwise, all the mono-vacancies are handled as neutral ones.

Firstly, we study the relaxation of the ionic positions due to the vacancy. For all these crystals with vacancy-type defect, we use a cubic supercell with  $2 \times 2 \times 2$  unit cells. In theoretically, the inward relaxation due to the vacancy should be obtained. However, after a careful test of convergence, there

exits a very little outward expansion for the size of the supercell except in the case of the mono-vacancy in Al (see the Table 2). One reason may be that we use the experimental lattice parameters as initial values and they are always a little smaller than the theoretical ones. Another reason may be that the supercell size is not large enough. While the nearest neighbour distance becomes short after relaxation in YH scheme and this is reasonable. At the same time, we calculate the positron lifetimes of vacancy-type defect in Al, 3C-SiC, GaAs and Si in NYH and YH scheme. Next, we study the effect of the localized positron on the relaxation of the electronic structure surrounding a vacancy by calculating the electronic structure of monovacancies in bulk Al, 3C-SiC, GaAs and Si with and without the localized positron, meanwhile, the ionic positions are kept fixed.

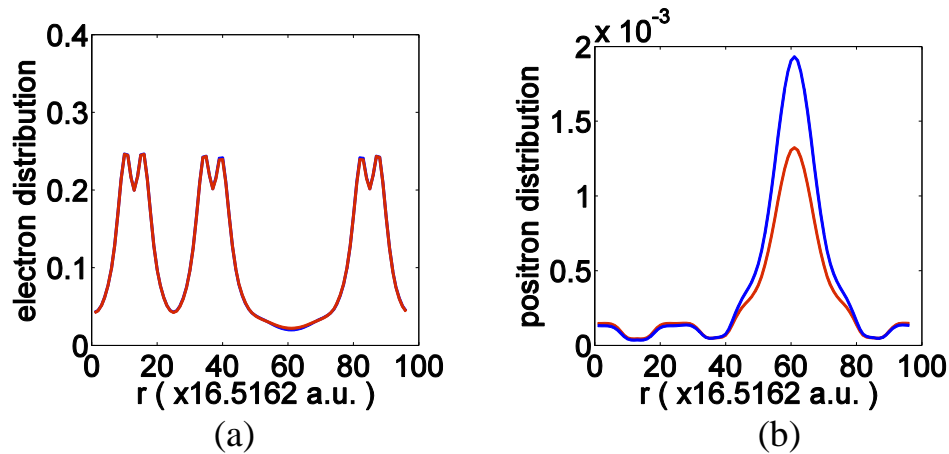
**Table 2.** The calculated lattice constants (in Å) and relaxations for the crystals with vacancy-type defect in NYH and YH scheme. A positive (negative) number denotes the outward (inward) relaxation in percentage of the nearest neighbour distance with respect to the ideal vacancy.

	<i>Al</i>	<i>3C_SiC</i>			<i>GaAs</i>		<i>Si</i>
	$V_{Al}$	$V_{Si}$	$V_C$	$V_C + C_{Si}$	$V_{Ga}$	$V_{As}$	$V_{Si}$
NYH	8.10	8.66	8.66	8.66	11.14	11.14	10.86
YH	8.06	8.75	8.74	8.81	11.46	11.48	10.90
Rel. (%)	-1.43	11.24	2.87	15.29	-8.85	-7.07	-6.97



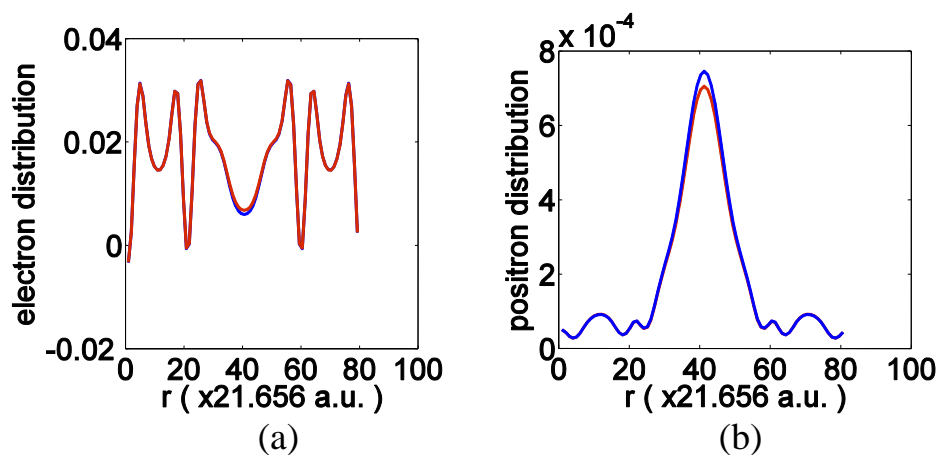
**Figure 2.** (color online) physical distribution of Al with monovacancy in [110] direction through the vacancy, the blue line denotes the distribution calculated in YH scheme and the red line denotes that calculated in YH+P scheme. (a) The electron density, (b) the trapping potential, (c) the positron density.

For mono-vacancy in aluminum, shown in Figure 2, the electron density inside the vacancy slightly increases, the positron potential becomes deeper, and the positron is more localized in YH+P scheme than that in YH scheme, so the positron lifetime becomes shorter further.



**Figure 3.** (color online) physical distribution of 3C-SiC with monovacancy of carbon in [110] direction through the vacancy, the blue line denotes the distribution calculated in YH scheme and the red line denotes that calculated in YH+P scheme. (a) The electron density, (b) The positron density.

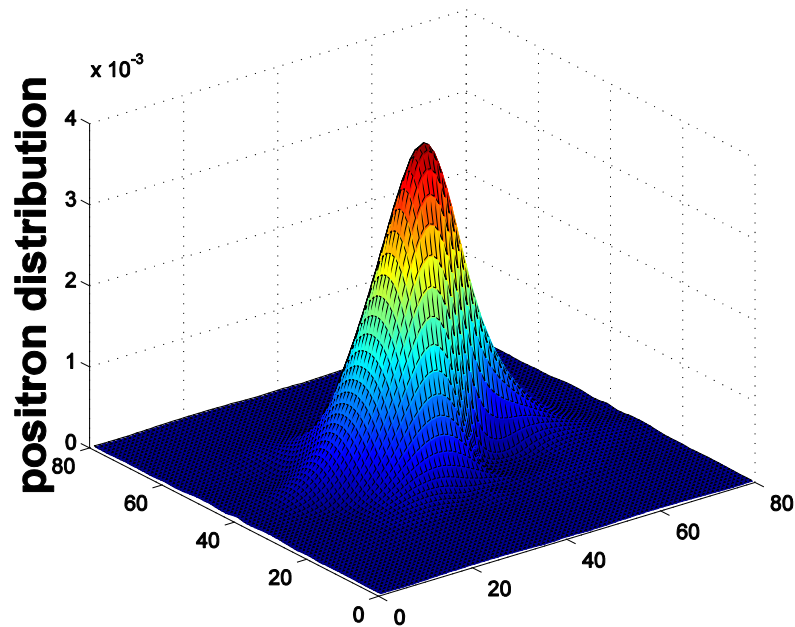
And for carbon mono-vacancy in SiC, its positron lifetime is controversial. In some previous theoretical studies, it was found that the carbon defect is not a positron trapping state. In our study, the electron density inside the vacancy almost remains unchanged and the positron becomes less localized, as shown in Figure 3 (a) and (b) respectively. The calculated positron lifetime is very close to its bulk lifetime, so we think the carbon vacancy can not be detected by the positron lifetime spectroscopy.



**Figure 4.** (color online) physical distribution of GaAs with monovacancy of gallium in [110] direction through the vacancy, the blue line denotes the distribution calculated in YH scheme and the red line denotes that calculated in YH+P scheme. (a) The electron density, (b) the positron density.

We also show the change of the electron and positron density inside the vacancy for the gallium vacancy in GaAs. As shown in Figure 4 (a) and (b), the electron density is just a little larger in YH+P

scheme than that in YH scheme, and the positron is a little less localized. But in NYH scheme, the positron is well localized, as shown in Figure 5.



**Figure 5.** (color online) the distribution of the positron density of GaAs with monovacancy of gallium in NYH scheme in [110] direction.

**Table 3.** Comparison of the monovacancy positron lifetime (in ps) calculated in NYH, YH and YH+P way. Different forms of the enhancement factor (BNLDA, APGGA and PSN) were used. The corresponding experimental values are obtained from the literatures.

Crystal	NYH	YH	YH+P	Exp.
	BNLDA/APGGA/PSN	BNLDA/APGGA/PSN	BNLDA/APGGA/PSN	
$Al\_V_{Al}$	242/219/276	235/212/265	221/194/243	244 <sup>a</sup>
$3CSiC\_V_{Si}$	187/191/192	214/219/225	198/188/203	188 <sup>b</sup>
$3CSiC\_V_C$	147/146/142	152/152/146	150/149/145	No <sup>c</sup>
$V_C + C_{Si}$	144/143/138	150/150/145	150/149/144	---
$GaAs\_V_{Ga}$	263/274/276	253/259/246	252/257/245	260 <sup>d</sup>
$GaAs\_V_{As}$	257/268/268	254/261/248	254/259/247	257 <sup>e</sup>
$Si\_V_{Si}$	254/252/259	235/233/230	233/230/227	282 <sup>f</sup>

<sup>a</sup> Corresponding experimental results within reference 12.

<sup>b</sup> Corresponding experimental results within reference 11.

<sup>c</sup> Corresponding experimental results within reference 13.

<sup>d</sup> Corresponding experimental results within reference 14.

<sup>e</sup> Corresponding experimental results within reference 15.

<sup>f</sup> Corresponding experimental results within reference 16.

We give the calculated positron lifetimes in different schemes and their corresponding experimental values in Table 3. The positron lifetimes do not change very much after we take the relaxation of the

ionic positions due to the vacancy and the electronic structure due to the presence of the positron. The positron lifetimes in NYH scheme are even much closer to the experimental ones, especially for the vacancy in silicon, we conclude that the effect of the relaxation of the electronic structure due to the positron may be less important than that of the relaxation of the ionic positions due to the positron in some cases. The studies on silicon with monovacancy [17-19] in fully self-consistent way give lifetimes around 270ps, this is very close to the experimental one, and clearly prove that the effect of the relaxation due to the vacancy can not be compensated by that of the relaxation due to the presence of the positron.

## 5. Conclusions

The positron lifetimes of monovacancies in crystals are studied in the conventional way and self-consistent way. For perfect crystals, the similar results are obtained in these two ways, and the results in the GGA form are much closer to the experimental ones. For monovacancies in crystals, we select three schemes to calculate the positron lifetimes. In YH+P scheme, the electron density inside the vacancy more or less increases due to the presence of the positron if the ionic positions are kept fixed, and after the relaxation of the electronic structure, the positron is more localized for the mono-vacancy in aluminum, while less localized for the Gallium mono-vacancy in GaAs and Carbon mono-vacancy in SiC. The results with no consideration of the relaxation are even more similar with the experimental ones, especially for silicon monovacancy in silicon, so we conclude that maybe the effect of the relaxation of the electronic structure due to the positron is less important than that of the relaxation of the ionic positions due to the presence of the positron in some cases, in other words, the effect of the relaxation due to the vacancy can not be compensated by that of the relaxation due to the presence of the positron in some cases.

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