

## *Ab Initio* Study of Positron Trapping at a Vacancy in GaAs

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We present a first-principles study of positron trapping at a negatively charged As vacancy in GaAs. Lattice relaxations induced both by the presence of the defect *and* of the positron have been included in a self-consistent way. In the presence of a positron, the volume of the vacancy increases and its symmetry is lowered. The positron wave function is well localized in the defect. Calculated positron lifetimes and angular correlations of annihilation photons are in good agreement with recent experiments.

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Positron annihilation experiments have recently emerged as a powerful method for the investigation of vacancy-type defects in semiconductors [1,2]. Experimental evidence shows that positrons can get trapped at neutral and negative vacancies, which result in a change of their annihilation characteristics, e.g., in an increase of their lifetime above the free recombination value [3]. Lifetimes can be related to the size of the vacancies, whereas angular correlations of annihilation radiation (ACAR) yield information about the momentum distribution of the electrons seen by the positron [4].

A detailed interpretation of positron annihilation experiments is very delicate in semiconductors where, at variance with metals, vacancies can have different charge states. Binary semiconductors pose special problems since vacancies can be formed in both sublattices, and negatively charged antisite defects may act as shallow positron traps [3]. For example, the identification of vacancy charge states in GaAs has been the subject of different interpretations over the past few years [5,6]. Moreover important properties of trapped positrons are not directly accessible to experiment; in particular, it is not known whether the presence of a positron modifies the shape and symmetry of the defect.

Several calculations of positron states at vacancies in semiconductors have appeared in the literature of the past few years [4,7–12]. None of them included self-consistently either electronic or ionic relaxations induced by the positron. Furthermore, the electronic charge was in most cases approximated by a sum of atomic charges [8–11]. In Ref. [8] a series of calculations carried out for different fixed geometries showed that positron lifetimes strongly depend on the volume of the vacancy, but that they are almost independent of its symmetry. Existing calculations indicate that a non-fully-self-consistent treatment of the interactions is inadequate in order to reproduce measured lifetimes.

In this Letter we present a first-principles study of positron trapping at a vacancy in a binary semiconductor, including lattice relaxations induced both by the

presence of the defect *and* of the positron. We investigated the case of a singly negative As vacancy ( $V_{As}^-$ ) in GaAs. Ionic forces, electronic, and positronic wave functions were calculated self-consistently on the basis of a two-component density-functional theory [13], using the Car-Parrinello (CP) approach [14]. Therefore no *a priori* assumption on the symmetry of the vacancy or on the positronic wave function was necessary. We found that the presence of a positron dramatically affects the size and the shape of the vacancy. Atoms rearrange so as to increase the volume of the defect, while lowering its symmetry. The formation of a weak bond between two Ga atoms similar to those found, e.g., in amorphous GaAs [15] is observed. The positron wave function is found to be localized in the vacancy, at a slightly off-center position. Calculated lifetimes and angular correlations of annihilation photons are in good agreement with experiment.

In our calculations the CP approach [14] for simultaneous optimization of electronic and ionic degrees of freedom was extended to include positronic degrees of freedom, within a two-component density-functional theory [13]. The electron-positron correlation was included within the local density approximation (LDA), according to the results of jellium model calculations by Arponen and Pajanne [16], as parametrized by Boroński and Nieminen [13]. No positron self-interaction was included, which is appropriate for the description of a single positron in an electron gas.

We adopted a plane-wave pseudopotential approach; the interaction between ionic cores and valence electrons was described by norm-conserving pseudopotentials [17] expressed in a separable form [18], with *s* and *p* nonlocality. The interaction between ionic cores and the positron was represented by a local pseudopotential [19]. The energy cutoffs used for the expansion of the electronic and positronic wave functions and of the charge density and potential were 13 and 52 Ry, respectively. We used a supercell containing 63 atoms (64 for the perfect crystal), with simple cubic periodic boundary conditions. The su-

percell Brillouin zone (BZ) was sampled with the  $\Gamma$  point only. The size of the cell corresponds to the calculated equilibrium volume of the crystal, i.e., to a lattice constant of 5.57 Å, to be compared with the experimental value [20] of 5.65 Å.

We first created a  $V_{As}^-$  vacancy in the GaAs crystal allowing the ions to relax in the absence of a positron. This leads to a lowering of the symmetry of the vacancy from  $T_d$  to  $D_{2d}$ . In agreement with recent total energy calculations [21], we find a strong inward relaxation of the vacancy's nearest neighbors. Two pairs of neighbors are formed, where Ga atoms get as close as 2.75 Å; this can be regarded as a weak bond, according to Ref. [15]. Each atom is then fourfold coordinated as in the perfect crystal. The atomic arrangement around the vacancy is shown in Fig. 1(a). We then added a positron to the system and computed self-consistently its ground state wave function and the electronic wave functions, without allowing any lattice relaxation. The positron wave function has its maximum at the vacancy center and it extends over a few bond lengths. A surface of constant positron density is shown in Fig. 1(b).

Finally, the system was fully relaxed by allowing the electronic wave functions and the ionic positions to readjust in the presence of the positron, starting from configurations close to that obtained in the absence of a positron. The full relaxation yields an energy gain of about 0.8 eV and leads to two minima with total energies differing by 0.016 eV. Within the accuracy of our calculation these two minima are degenerate. The corresponding ionic configurations are shown in Figs. 1(c) and 1(e): they have different symmetries,  $C_{2v}$  and  $C_s$ , but very similar physical properties. In both cases the volume of the vacancy is increased significantly with respect to that found in the absence of a positron, and it becomes comparable to the volume of the ideal vacancy. The distances between Ga atoms and the center of the vacancy range from 2.14 to 2.61 Å in the  $C_{2v}$  geometry and from 2.23 to 2.49 Å in the  $C_s$  geometry. These are to be compared with a distance of 2.41 Å in the ideal vacancy configuration, and of 2.04 Å in the  $D_{2d}$  geometry. In both the  $C_{2v}$  and  $C_s$  minima, the two pairs of first Ga neighbors are not equivalent; the distances between the Ga atoms of one pair are 2.49 and 2.64 Å in the  $C_s$  and  $C_{2v}$  geometries, respectively, whereas the distances between the atoms of the other pair are 4.00 and 4.16 Å. Therefore only one of the Ga pairs is bonded, at variance with the equilibrium configuration obtained in the absence of a positron. Our results demonstrate the importance of a self-consistent treatment of ionic and electronic relaxations, taking into account the presence of the positron.

An upper bound to the energy barrier between the  $C_{2v}$  and the  $C_s$  configurations was determined from a series of total energy calculations carried out for intermediate ionic configurations; these are defined by the coordinates

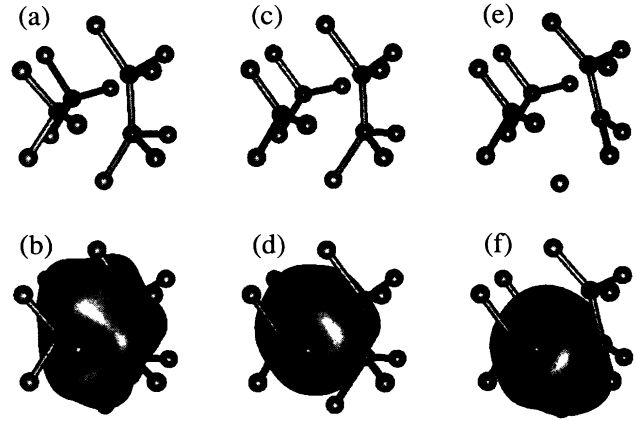


FIG. 1. Positions of the vacancy first and second neighbors and positronic charge densities ( $n_+$ ) in the  $D_{2d}$  (a),(b),  $C_{2v}$  (c),(d), and  $C_s$  (e),(f) configurations. Two atoms are represented as bonded if their distance is less than 2.8 Å. The surface of constant positronic density  $n_+ = 2.2 \times 10^{-4}$  a.u. is represented. The maximum of  $n_+$  is  $5.8 \times 10^{-3}$ ,  $1.2 \times 10^{-2}$ , and  $10^{-2}$  a.u. in the  $D_{2d}$ ,  $C_{2v}$ , and  $C_s$  configurations, respectively.

$\mathbf{R}(\alpha) = \mathbf{R}_{C_{2v}} + \alpha(\mathbf{R}_{C_s} - \mathbf{R}_{C_{2v}})$ , where  $\mathbf{R}_{C_{2v}}$  and  $\mathbf{R}_{C_s}$  denote the ionic coordinates in the  $C_{2v}$  and  $C_s$  geometries, respectively. Five values of the parameter  $\alpha$  between zero and 1 were considered. The highest energy barrier along this path is 0.03 eV. We therefore expect both the  $C_{2v}$  and the  $C_s$  geometries, together with the intermediate configurations, to be present at room temperature.

In both the  $C_{2v}$  and the  $C_s$  geometries, we find that the positronic wave function is well localized in the vacancy, at a slightly off-center position, as shown on Figs. 1(d) and 1(f). In both configurations, the maximum of the positron charge density is nearly twice as large as in the unrelaxed  $D_{2d}$  geometry [Fig. 1(b)]. We note that in the ideal unrelaxed vacancy ( $T_d$  symmetry) the positron is as localized as in the  $C_{2v}$  and  $C_s$  configurations; however, the total energy of the  $T_d$  configuration is about 0.5 eV higher than those of the  $C_{2v}$  and  $C_s$  minima. As a general rule, we find that the degree of localization of the positronic wave function is related to the volume of the vacancy: larger vacancies allow for a better localization of the positron.

Positron lifetimes ( $\tau$ ) were calculated in all of the above configurations following the approach of Jensen [22]:

$$1/\tau = \pi r_0^2 c \int n_+(\mathbf{r}) n_-(\mathbf{r}) g_0(n_-) d\mathbf{r}. \quad (1)$$

Here  $r_0$  is the classical radius of the electron,  $c$  the speed of light, and  $n_+$  and  $n_-$  denote the positronic and electronic charge densities, respectively.  $g_0$  is the contact density (i.e., the value at the origin of the electron-positron pair correlation function) consistent with the results of Arponen and Pajanne [16] used in our calculation for the electron-positron correlation energy. In

TABLE I. Experimental [6] and theoretical positron lifetimes for the perfect crystal and for the  $V_{As}^-$  vacancy (in ps).  $D_{2d}$ ,  $C_{2v}$ , and  $C_s$  denote the symmetries of the ionic configurations of  $V_{As}^-$ . Calculations have been performed by considering only the valence contribution ( $n_v$ ) to the electronic charge density  $n_-$ , and by including also the core contribution ( $n_c$ ). Fits for the core charge introduce inaccuracies of  $\pm 4$  ps.

Experiment	Bulk	$V_{As}^-$		
	$231 \pm 3$	$257 \pm 3$		
Theory	Bulk	$D_{2d}$	$C_{2v}$	$C_s$
$n_- = n_v$	229	237	273	279
$n_- = n_v + n_c$	200	207	254	261

Table I the positron lifetimes computed in the perfect crystal and in various geometries of the  $V_{As}^-$  vacancy are compared with the experimental values of Saarinen *et al.* [6]. The lifetimes calculated in the fully relaxed vacancies ( $C_{2v}$  and  $C_s$ ) are significantly longer than in the perfect crystal, in agreement with experimental results. Furthermore, the lifetime calculated in the unrelaxed  $D_{2d}$  configuration—which has the smallest volume—is close to that found in the perfect crystal. These conclusions remain unchanged if the core electrons' contribution is included in  $n_-$ , although the net effect of electronic core charges on positron lifetimes is important. We note that the difference in lifetimes between the bulk and the fully relaxed vacancy configurations is overestimated in our calculations. We checked the influence of the plane-wave energy cutoff and of the BZ sampling on the bulk lifetime by repeating our computations with a 64 atom supercell and  $E_{cut}=18$  Ry, and with a 128 atom supercell (corresponding to an improved BZ sampling) and  $E_{cut}=13$  Ry. In both cases the result differed by less than 0.5% from that reported in Table I. Positron lifetimes could also be affected by the local density approximation used for the electron-positron correlation energy  $E_c^{e-p}$ , and by the parametrization of the contact density and of  $E_c^{e-p}$ . It would be of interest to investigate the effect of the LDA by means, e.g., of quantum Monte Carlo calculations.

In all of the configurations of  $V_{As}^-$ , the calculated lifetimes correlate well with the size of the vacancy and with the degree of localization of the positron wave function. They do not, however, depend sensitively on the symmetry of the vacancy, as can be seen in Table I, where lifetimes calculated in the  $C_{2v}$  and the  $C_s$  configurations are quite similar. This is consistent with the results of Ref. [8]. Our findings support the current interpretation of increased positron lifetime as a signature of positron trapping at a vacancy [1,2]. However, one can prepare well localized positronic states which have lifetimes of the order of the free recombination value. For example, by starting from a positronic wave function localized in an interstitial region in the perfect crystal, and by relaxing electronic and positronic degrees of freedom, we found a minimum energy configuration in which the positronic

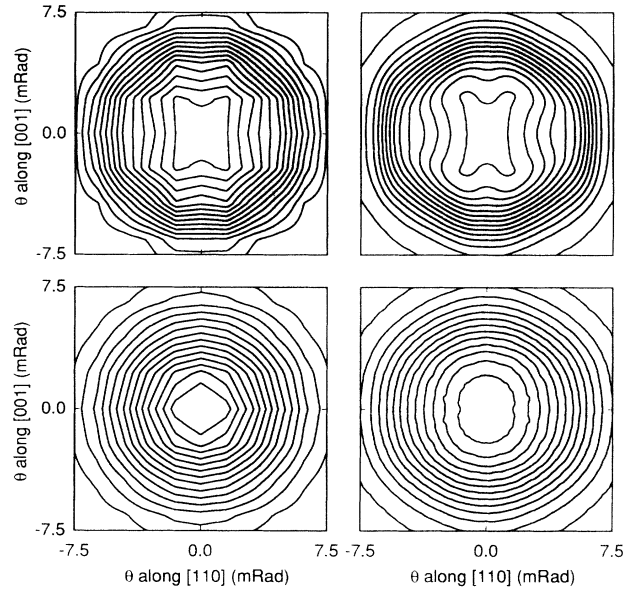


FIG. 2. Calculated (left panels) and experimental [23] (right panels) angular correlations of annihilation photons integrated along  $[1\bar{1}0]$  for the perfect crystal (upper panels) and the  $V_{As}^-$  vacancy (lower panels). Experimental results were extracted from ACAR spectra measured on a semi-insulating single crystal and on a Si doped ( $n$ -type, with  $6.2 \times 10^{16}$  carriers/cm<sup>3</sup> at 300 K) single crystal. The momenta  $p_i$  are related to the measured angles  $\theta_i$  by  $p_i = m_e c \sin \theta_i \simeq m_e c \theta_i$ .

wave function is as localized as in the  $C_{2v}$  and  $C_s$  configurations. Yet its lifetime is very close to the free recombination value, i.e., to the lifetime calculated for an extended positronic wave function in the bulk (see Table I). We note that the two bulk configurations having extended and localized positronic wave functions have very close total energies, suggesting that positron self-trapping in a perfect crystal might be possible. Further investigations on this issue would, however, require the use of very large supercells and are beyond the scope of this Letter.

Further comparison with experiment is provided by computing the momentum distribution of the positron annihilation rate  $[\rho(\mathbf{p})]$ , which is related to measured ACAR spectra. We computed  $\rho(\mathbf{p})$  as

$$\rho(\mathbf{p}) = \frac{\pi r_0^2 c}{V} \sum_i^N \left| \int e^{-i\mathbf{p} \cdot \mathbf{r}} \sqrt{g_0(n_-)} \psi^+(\mathbf{r}) \psi_i^-(\mathbf{r}) d\mathbf{r} \right|^2. \quad (2)$$

$V$  is the volume of the supercell,  $\psi^+$  denotes the positronic wave function, and  $\psi_i^-$  the  $N$  occupied valence electronic states. Figure 2 shows  $\rho(\mathbf{p})$  integrated along the  $[1\bar{1}0]$  direction as calculated for the perfect crystal (extended positron wave function) and for the fully relaxed  $C_{2v}$  vacancy. In agreement with recent experimental results [23] also shown in Fig. 2, we find that the central peak of the distribution is much narrower in the presence of the vacancy than in the perfect crystal.

The distributions  $\rho(\mathbf{p})$  calculated in the  $C_{2v}$  and in the  $C_s$  configurations are indistinguishable, showing that the electronic structure of the  $V_{As}^-$  vacancy in both configurations is very similar.

The choice of the energy functional used in our calculations deserves some comments. We used a functional which explicitly excludes spurious positron self-interactions, since the Arponen and Pajanne (AP) expression [16] for the correlation energy density does not depend on the positron density. This is the correct description of *one* positron interacting with an electron gas, since such a positron *does not* interact with itself. On the contrary, in the formulation proposed by Boroński and Nieminen [13] for a two-component electron-positron plasma, the correlation potential acting on the positron depends explicitly on the positron density, inducing a self-interaction term. In this formulation, all other positron self-interaction terms have therefore to be included in the Hamiltonian in order to have a proper cancellation of terms. We have repeated some of the calculations described above within the Boroński and Nieminen [13] formulation. The minimum energy configuration for the  $V_{As}^-$  vacancy obtained in this way differs from that calculated with the AP functional. The equilibrium geometry resembles closely the one obtained in the absence of a positron ( $D_{2d}$  symmetry), the positron wave function extends over the whole supercell, and positron lifetimes do not show any significant increase above the free recombination value. Therefore, as expected, a proper treatment of positron self-interaction terms turns out to be very important in situations where the positron wave function is localized, as in the vacancy studied here.

In conclusion, we have presented the first fully self-consistent calculation of positron trapping at a vacancy in a binary semiconductor. In particular, we have shown that a positron induces large ionic relaxations around a singly negative As vacancy in GaAs, thereby lowering its symmetry and increasing its volume. The positron wave function is well localized in the defect. Calculated positron lifetimes and angular correlations of annihilation photons show good agreement with available experimental data.

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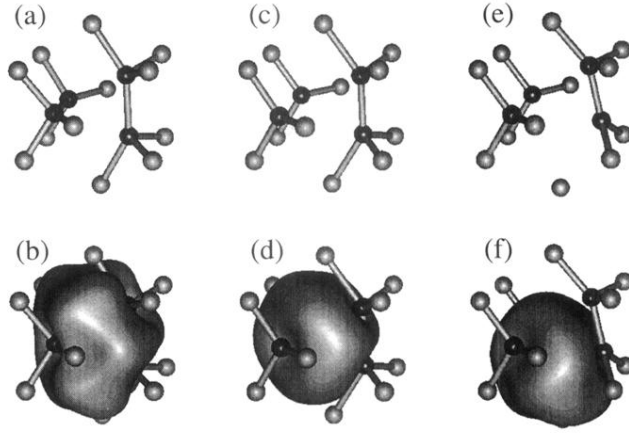


FIG. 1. Positions of the vacancy first and second neighbors and positronic charge densities ( $n_+$ ) in the  $D_{2d}$  (a),(b),  $C_{2v}$  (c),(d), and  $C_s$  (e),(f) configurations. Two atoms are represented as bonded if their distance is less than 2.8 Å. The surface of constant positronic density  $n_+ = 2.2 \times 10^{-4}$  a.u. is represented. The maximum of  $n_+$  is  $5.8 \times 10^{-3}$ ,  $1.2 \times 10^{-2}$ , and  $10^{-2}$  a.u. in the  $D_{2d}$ ,  $C_{2v}$ , and  $C_s$  configurations, respectively.