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1991 J. Phys.: Condens. Matter 3 7217

(http://iopscience.iop.org/0953-8984/3/37/015)

J. Phys.: Condens. Matter 3 (1991) 7217–7224. Printed in the UK

LETTER TO THE EDITOR

Charge-state-dependent relaxation and positron states at vacancy defects in GaAs

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Received 5 July 1991

Abstract. The positron states in the perfect GaAs lattice and at fully relaxed vacancies with different total charges have been calculated. Moreover, the metastable configuration of the As anti-site in GaAs proposed as a model for the EL2 defect is considered. The atomic structures of the defects are taken from recent *ab initio* molecular dynamics calculations. The positron states and the ensuing positron annihilation rates and trap binding energies have been determined by the method based on the superposition of atomic electron densities. A comparison of the results with experimental data shows that, while the present theoretical approach gives a consistent and qualitative interpretation, it fails to reproduce the trapped state lifetimes quantitatively. It is shown that a localized positron can affect the lattice relaxations around the defect. Therefore, it is suggested that the positron should be treated fully self-consistently, simultaneously with electrons, in the *ab initio* molecular dynamics in order to determine the way in which the localized positron affects the electron structure and ionic relaxation near the vacancy.

Positron lifetime spectroscopy has established itself as a useful method for studying defects in semiconductors [1–4]. The method is especially powerful for vacancy-type defects at which localized positron states exist due to the reduced repulsion from the positive ions. The value of the positron lifetime is very sensitive to the changes in the open volume available for the positron [5], and therefore the changes seen in the positron lifetime have been connected with the changes in the ionic positions (i.e. relaxation) around the defect. For example, the two lifetimes of 295 and 258 ps in n-type GaAs samples have been interpreted as arising from positrons trapped at neutral and singly negative As vacancies which have very different relaxations [4]. Another example is the EL2 defect in GaAs. Positron lifetime measurements [3] indicate that the metastable state of this defect has an open volume which is able to trap a positron, but that the open volume should be smaller than that for a vacancy.

We have recently studied the electronic properties and the corresponding ionic relaxations of vacancies in GaAs [6]. The calculations were performed by using the so-called Car–Parrinello method [7] which combines density-functional theory and molecular dynamics giving both the electronic structure and the ionic positions without any empirical parameters. Only modest relaxations were found for the Ga vacancies in different charge states and for the As vacancy in the neutral state. In contrast, the singly and doubly negative As vacancies were found to have a strong inward relaxation for the ions nearest to the vacant site. As discussed in our previous article [6], the theoretical results for the relaxations are in good qualitative agreement with the

0953-8984/91/377217+08$03.50

positron lifetime measurements. In this letter we will make a quantitative comparison using the calculated positron lifetimes and enlarge our discussion to a metastable configuration of the As anti-site in GaAs, which is one of the models suggested [8] for the famous EL2 defect in GaAs.

Our present calculations of positron states are based on the standard local density scheme [9], in which the electron structure of the solid without the influence of the positron is calculated first. The potential sensed by the positron consists of two parts: (i) the Coulomb contribution due to the nuclei and the electron density distribution; and (ii) the correlation potential which mimics the energy decrease due to the accumulation of screening electron charge near the positron. The positron state is then solved from a one-particle Schrödinger equation and finally the positron annihilation rate is calculated by integrating the product of the positron density and the local annihilation rate over the crystal volume. The positron correlation potential and the annihilation rate are treated in the local density approximation (LDA) [9, 10], i.e. at a given point they are functions of the total electron density at that point only. The correlation and annihilation functions are based on the calculations for a positron in a homogeneous electron gas [11]. Moreover, the imperfect screening of the positron in the semiconductor is taken into account by including in the positron correlation potential and annihilation rate a semi-empirical reduction factor [13, 9]. We would like to stress that the calculation method described earlier has no parameters adjusted to measured positron lifetimes. Later we will introduce a scheme which has one parameter for the localized states.

For the delocalized positron states, the approach used can be justified by the two-component density-functional theory [14]. However, in the case of a localized positron the two-component theory asserts that the positron should influence (increase) the *average* electron density near the trap, and a simultaneous calculation of the electron and positron densities is required. Moreover, because the electron structure is affected by the positron, the ionic structure is also expected to change. However, the conventional scheme has been supported by the view that the positron and its screening cloud form a neutral quasi-particle which does not cause a long-range disturbance in the electron structure of the solid.

Our Car–Parrinello calculations [6] use the supercell approximation. For a vacancy the supercell contains 63 atoms and one vacant site, i.e. the supercell is a cube with the edge length of two lattice constants. Periodic boundary conditions are imposed through the surface of the supercell. The calculation of the electron structure is based on the use of the pseudopotentials for the ion cores and the pseudo valence electron density is obtained as a plane wave expansion. The Car–Parrinello calculation simultaneously finds the ground-state positions of the atoms and the corresponding electron density by the simulated annealing method.

In order to calculate the positron states, the *total* electron density of the solid is needed instead of the pseudo valence electron density. Here we rely on the method of superimposed atoms [15]. A supercell with atomic positions given by the Car–Parrinello calculations is introduced. The supercell is then divided into a calculational mesh with $32 \times 32 \times 32$ points forming a simple cubic lattice. The total electron density and the Coulomb potential at the mesh points are obtained by superimposing free atom profiles. The potential felt by the positron is then calculated at the mesh points and the positron wavefunction with periodic supercell boundary conditions is found by a relaxation method. Finally the positron annihilation rate is calculated by numerical integration in the mesh.

According to the current understanding [12] the relaxation of a vacancy in a semiconductor depends on the charge state of the vacancy through the number of localized electrons in the deep levels in the band gap. In the case of GaAs, a neutral Ga vacancy has three electrons in the deep levels whereas a neutral As vacancy has only one electron. The occupation of the deep levels depends on the position of the Fermi level. When there are no electrons in the deep levels the relaxation is symmetry conserving, i.e. there is only a breathing component in the relaxation. If there is one electron on a deep level a tetragonal relaxation connected with the Jahn–Teller effect lowers the symmetry so that the atoms nearest the vacancy move closer to each other: there is a pairing component in the relaxation. The second electron added can, due to spin degeneracy, occupy the same spatial state as the first one. Therefore the symmetry does not change but the magnitude of the relaxation is usually larger. Figure 1 shows the displacements of the atoms nearest the vacancy in this case. The total displacement is divided into a breathing (b) and a pairing (p) component. The third bound electron has to occupy a spatially different state from the two previous ones and it causes a further lowering in the symmetry. The relaxation is a mixture of tetragonal and trigonal relaxations and the displacements cannot any longer be described by the two-vector scheme of figure 1.

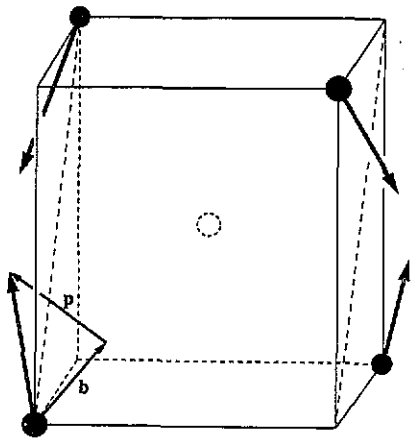

Figure 1. The nearest-neighbour relaxations associated with tetragonally relaxed vacancy in a semiconductor. The components of one relaxation vector are shown; b denotes the breathing mode and p the pairing mode. They both lie in the (110) plane shown. The directions of the vectors correspond to the negative As vacancy calculated in [6] but the lengths are scaled by a factor of 2.5.

According to our earlier Car–Parrinello calculations [6] the atoms neighbouring a Ga vacancy relax slightly inwards and the relaxation is insensitive to the charge state of the vacancy. The breathing components b for the neutral (V^0_{Ga}), singly negative (V^-_{Ga}) and doubly negative (V^{2-}_{Ga}) charge states are -3.9%, -2.9% and -3.8% of the bond distance, respectively (the minus sign denotes the *inward* relaxation). The displacements perpendicular to the breathing component are small (less than 2%). The neutral As vacancy (V^0_{As}) has a small outward relaxation whereas in the case of the negative (V^-_{As}) and the doubly negative (V^{2-}_{As}) As vacancies the four nearest-neighbour Ga atoms move strongly towards the centre of the vacancy. The breathing relaxation components are $+2.0\%$, -16.4% and -17.4%, respectively. As a matter of

fact, the directions of the relaxation vectors, and those of the breathing and pairing components correspond to the negative As vacancy in GaAs. The pairing components p defined in figure 1 are −0.6%, −17.0% and −15.6%, respectively. In the case of V_{As}^{2-} there is also a small relaxation component perpendicular to b and p (three electrons in the deep levels). The strong relaxation for the negative As vacancies results from bond formations between the Ga atoms in the two pairs. Because the relaxations for Ga vacancies in all charge states are very similar, as are those for the various negative As vacancies, we have made positron calculations only for the neutral Ga vacancy and for the neutral and negative As vacancy. Here one should note that according to calculations [16] using self-consistent electron structures of vacancies in semiconductors the positron lifetime is somewhat insensitive to the charge state of the vacancy if the atomic positions are kept the same in the different charge states.

Table 1. Positron annihilation characteristics for the perfect GaAs lattice and for the different vacancy-type defects. The calculated positron annihilation rates with core (λ_c) and valence (λ_v) electrons, the positron lifetime ($\tau = 1/(\lambda_c + \lambda_v)$), and the positron binding energy (E_b) are given. The experimental results τ^{exp} for the positron lifetime are also shown.

Vacancy	λ_c (ns^{-1})	λ_v (ns^{-1})	τ (ps)	E_b (eV)	τ^{exp} (ps)
Bulk GaAs	0.533	3.933	224	—	231[b]
V_{Ga}	0.424	3.797	237	0.17	260[a]
V_{As}	0.453	3.506	253	0.28	295[b]
V_{As}^{-}	0.521	3.880	227	0.	258[b]
As_{Ga}^{*}	0.350	3.976	231	0.20	255[c]

[a] Values from [19, 20].
[b] Values from [1, 4].
[c] Values from [3].

The calculated positron annihilation rates and binding energies for the different vacancies are given in table 1 along with the results for the perfect GaAs lattice. The calculated positron bulk lifetime, i.e. the lifetime for the perfect lattice, is slightly lower than the experimental value. This discrepancy arises from the use of the non-self-consistent electron density [9]. In the case of the different vacancies the theoretical positron lifetimes are considerably lower than the experimental ones. This is connected with the low positron binding energies at the traps. As a matter of fact the negative As vacancy hardly binds the positron at all: the supercell calculation gives nearly equal energy eigenvalues for the positron in the perfect lattice and for the lattice containing one vacancy in each supercell. Therefore the binding energy is zero in table 1. However, in spite of the overall values, which are too small, the differences between the theoretical positron lifetimes for different vacancies show the same trends as the experimental ones. The positron lifetime is longest for the neutral As vacancy and decreases by about 30 ps when the charge state changes to singly negative. Moreover, according to both experiment and theory the positron lifetime for the Ga vacancy is remarkably lower than that for the neutral As vacancy.

We have also tried to use the calculated self-consistent pseudo valence electron densities in the positron state and lifetime calculations as well. The pseudo valence electron density superimposed with the free atom core electron densities does not, however, give a proper Coulomb potential near the ion cores. The potential does

not rise strongly enough and therefore the positron density is too large in the high electron density region. The positron lifetimes become shorter than in the atomic superposition although the use of self-consistent electron densities should increase the positron lifetime [9]. For example, the positron bulk lifetime calculated in this way is 222 ps and the lifetime for a neutral As vacancy is 243 ps. If the Coulomb potential is taken from the atomic superposition and the self-consistent pseudo valence electron density is used only in the calculation of the correlation potential and the positron annihilation rate, a better agreement with earlier positron state calculations using self-consistent total valence electron densities [9] results. The results of this 'hybrid' scheme are 230 ps for bulk and 260, 231 and 242 ps for the neutral and singly negative As vacancy and for the neutral Ga vacancy, respectively. According to LMTO-ASA calculations [9] the positron bulk lifetime in GaAs is 231 ps and the lifetimes at neutral unrelaxed (ideal) As and Ga vacancies are 263 and 262 ps, respectively.

According to table 1, it is clear that the present theory does not give enough binding for the positron for localized states. This signals that the localized positron does affect its electronic and ionic environment. We have demonstrated the effects of the localized positron on the ionic relaxation in the case of the neutral As vacancy by calculating the total energy of the ion–electron system (elastic energy) as a function of the magnitude of the breathing relaxation component. We move only the four Ga atoms nearest to the vacancy. Simultaneously, we calculate the corresponding behaviour of the positron energy eigenvalue. The changes in the pairing component are not considered because the pairing relaxation is weak for the equilibrium configuration. The results are shown in figure 2(a) by broken curves. The elastic energy is parabolic around the equilibrium relaxation of +2% whereas the positron energy decreases when the relaxation increases. The total energy, the sum of the elastic (lattice) energy and the positron eigenenergy, is given in figure 2 as a full curve. It shows a minimum at a relaxation of about +6% which is clearly larger than the equilibrium relaxation of the 'clean' vacancy. The behaviour of the positron lifetime as a function of the breathing relaxation is shown in figure 2(b). It is seen that the change of relaxation from +2% to +6% increases the positron lifetime by around 15 ps. Thus, this calculation shows that the localized positron may change the relaxation around the defect remarkably and that the change can be seen as an increase in the positron lifetime.

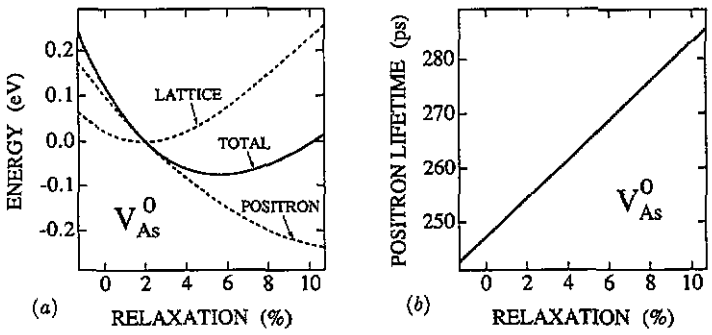

Figure 2. (a) The energies of a neutral As vacancy in GaAs. The energy of the ion–electron system or the elastic energy (LATTICE), the positron energy eigenvalue (POSITRON), and the sum of these two (TOTAL) are given as a function of the breathing mode relaxation given as a percentage of the bond distance. (b) The positron lifetime in a neutral As vacancy in GaAs as a function of the breathing mode relaxation.

The calculation for the positron localized at the neutral As vacancy described earlier should, however, be considered as a qualitative one. This is because different approximations have been used in the various parts of the calculations, and the corresponding errors introduced do not necessarily cancel. Moreover, the generalization of this treatment, for example, to the case of the negative As vacancy is difficult because the pairing component of the relaxation should also be considered. The complete solution to the problem could be, for instance, the adaption of the positron state into the Car–Parrinello method within the two-component density functional theory. This is a very demanding task and we have to postpone its execution. However, we can easily mimic the consequences of the enhanced binding (localization) by fictitiously increasing the mass of the trapped positron. After some experimentation we found that an effective positron mass of 1.5 times the free positron mass reproduces on average the experimental positron lifetimes for different vacancies rather well. By coincidence, this is the value of the effective positron mass which gives good agreement between the theoretical and experimental positron diffusion constants in solids [17]. The results are collected in table 2. The positron binding energies are given relative to the energy of the bulk state with the free positron mass. The binding energies at the vacancies in GaAs are now of the order of 1 eV, which is considerably more than the values given in table 1 for the effective mass of unity. The calculated positron lifetimes for the neutral and negative As vacancies are about 10 ps lower than the experimental ones given in table 1. The use of self-consistent electron densities would increase the theoretical values and decrease the discrepancy. The positron lifetime for the Ga vacancy is slightly longer than the experimental value. This discrepancy is expected to increase if self-consistent electron densities were to be used. The positron densities corresponding to the different vacancies in GaAs are shown in figure 3. The localization of the positron density is much stronger for the neutral As and Ga vacancies than for the singly negative As vacancy.

Table 2. Positron annihilation characteristics for different vacancy-type defects in GaAs. The results are obtained by using the positron effective mass of 1.5 times the free positron mass. The calculated positron annihilation rates with core (λ_c) and valence (λ_v) electrons, the positron lifetime ($\tau = 1/(\lambda_c + \lambda_v)$), and the positron binding energy (E_b) are given.

Vacancy	λ_c (ns^{-1})	λ_v (ns^{-1})	τ (ps)	E_b (eV)
V_{Ga}	0.216	3.565	264	0.93
V_{As}	0.273	3.213	287	1.00
V_{As}^{-}	0.327	3.714	247	0.67
As_{Ga}^{*}	0.287	3.721	250	0.67

Finally, we have calculated the positron state for an As anti-site defect (A_{Ga}^{*}) in GaAs in a metastable ionic configuration. According to the model by Dabrowski and Scheffler [8] this defect, in which the As atom is relaxed about 1.3 Å from the vacancy centre to the [111] direction, is the metastable state of the important EL2 defect. We have used the atomic positions calculated by Kaxiras and Pandey [18]. The use of the positron effective mass of unity gives a weakly bound state and a positron lifetime which is only slightly longer than the bulk lifetime (see table 1). But when the positron effective mass is 1.5, the open space at the defect is large enough

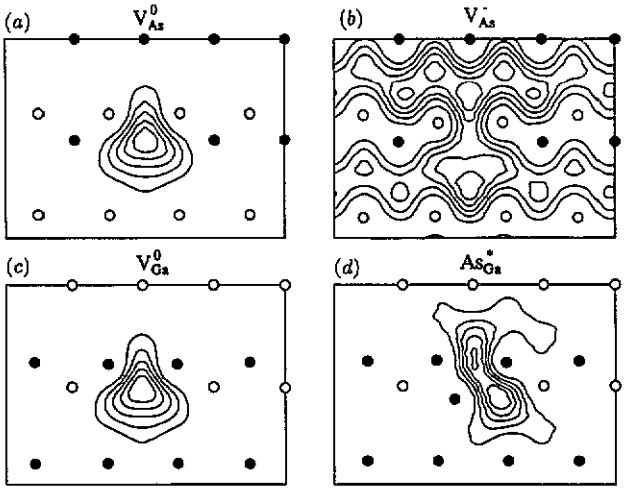

Figure 3. The positron densities for different vacancy-type defects in GaAs: (*a*) Ga vacancy; (*b*) neutral As vacancy, (*c*) singly negative As vacancy and (*d*) As antisite in the metastable relaxed state. The results correspond to the positron effective mass of 1.5 times the free positron mass. The figure shows a region of the (110) plane limited by the boundaries of the supercell. The contour spacing is one sixth of the maximum value. The full dots are the As atoms and the open ones are the Ga atoms.

to bind the positron strongly (see table 2 and figure 3(*d*)). The predicted positron binding energy and lifetime in this case are 0.84 eV and 250 ps, respectively. These numbers lie between the theoretical results for the negative As and Ga vacancies. The theoretical lifetime for As^*_{Ga} should be contrasted with the recent positron lifetime measurements [3] which indicate that the EL2 defect traps positrons in the metastable state, the positron lifetime being 255 ± 8 ps.

In conclusion, in this work we have calculated the positron states at defects in semiconductors using the latest first-principles results for defect structures. Our results for positron lifetimes show that the theoretical structures of the defects can explain the differences seen in the positron lifetimes measured for different types of defects. This is very encouraging for future theoretical work. However, the present state of the positron calculations is unsatisfactory: the effects caused by a localized positron on the electronic and ionic structure of the defect should be taken self-consistently into account to obtain a full quantitative theory for shallow positron traps in semiconductors.

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