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LETTER TO THE EDITOR

Positron annihilation at paramagnetic defects in semiconductors

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Abstract. Positron annihilation at vacancies in semiconductors is studied. We are interested in the formation of singlet and triplet positron–electron states, and especially, in their influence on the positron annihilation characteristics. These states are formed by a positron trapped by the vacancy and an unpaired (paramagnetic) electron in a deep level. We provide examples by determining the two ensuing positron lifetime components for vacancies in Si and GaAs. For the practical calculations it is shown how the self-consistent electron structures obtained by the pseudopotential–plane wave methods can be used. Finally, the implications are discussed from the experimental point of view.

Positron lifetime spectroscopy has become a powerful method for the study of vacancy-type defects in semiconductors [1–4]. On the basis of experimental and theoretical evidence the lifetime of positrons trapped by a vacancy-type defect depends strongly on the open volume available, i.e., on the positions (relaxations) of the nearest atoms around the defect. The measured positron lifetimes can change strongly between the different charge states of a defect. For example, the ionization process $V_{As}^{0} \rightarrow V_{As}^{-}$ for the As vacancy in GaAs causes a lifetime decrease of 37 ps [4]. Similarly, changing the charge state of a phosphorous–vacancy pair in Si from neutral to negative decreases the positron lifetime by 18 ps [3]. First-principles electron-structure calculations for vacancies in GaAs [5] have shown that the relaxations can indeed change between adjacent charge states appreciably, on the order of several per cent of the nearest-neighbour distance in bulk. Moreover, the calculated positron lifetimes [6] corresponding to the theoretical atomic structures of the vacancy-type defects in GaAs are in qualitative agreement with experiment.

In this paper we discuss another effect, which may influence positron lifetimes at vacancies in semiconductors. To begin with, we recall from quantum electrodynamics the selection rules for the annihilation of a positron–electron pair. In short, a two-gamma annihilation is possible when the positron and the annihilating electron are in a mutual spin singlet ($S = 0$, para) state but it does not occur in the triplet ($S = 1$, ortho) state. The remaining possibility for the ortho state—the three-gamma annihilation—has a much smaller rate. This effect is very familiar from studies of the electron–positron hydrogenic bound state, the positronium (Ps) atom. In vacuum, the para state has the shorter lifetime of 125 ps, whereas the ortho state lives for 142 ns [7]. In condensed matter, the lifetime of the ortho state of the Ps atom is suppressed by annihilation due to the 'spectator' electrons in the medium [8]. However, the ensuing 'pickoff' rate is usually small enough (lifetime of the order of 1–2 ns) to make the ortho state easily observable [7]. A relevant example is

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positron annihilation at F-centres in alkali halides [8]. Positrons get trapped at the colour centres (negative ion vacancies) where they form a highly correlated, Ps-like state with the excess electron. The ortho component of this state is long-lived, eventually dying through the pickoff channel.

In metals or semiconductors the electronic screening is efficient and the electron–positron interaction does not result in a bound state. For spin-compensated electronic systems there is no direction of reference for the positron spin and only one lifetime component results either for a free positron or a positron trapped at a vacancy. The annihilation rates in these cases are successfully described by the local density approximation (LDA) [9,10]. However, at semiconductor vacancies Ps-like states can be formed. The prerequisite is that there is an odd number of electrons in the bound gap states, in which case the electron with the highest energy is *unpaired*, i.e. it has no pair with opposite spin on the same orbital wavefunction. This kind of defect is often called paramagnetic because it can be observed by the electron paramagnetic resonance technique [11]. Consequently, in the following we will call the ensuing effect 'the paramagnetic effect' in positron annihilation. The unpaired electron and the positron trapped by the vacancy form a two-body system, in which their spins can be either parallel or antiparallel. As a result, the positron annihilation in a paramagnetic vacancy leads to two lifetime components as in Ps annihilation. The difference is that the force keeping the electron and positron together originates now from the existence of a vacancy in the semiconductor lattice, whereas Ps is held together by the Coulomb attraction between electron and positron. This fact also distinguishes the Ps-like states at vacancies in semiconductors from the various other cases where quasipositronium is observed in solids [8]. The main aim of this work is to estimate if the para and ortho states can be distinguished experimentally also in the case of paramagnetic vacancies in semiconductors.

The efficient electronic screening in semiconductors manifests itself also in the fact that the calculated total electron density at a vacancy does not change very much between different charge states, as long as the atomic relaxation does not change. This is in turn reflected in the insensitivity of the calculated positron lifetimes to the charge state for ideal (unrelaxed) vacancies in semiconductors [12,13]. The paramagnetic effect discussed in this paper brings a new kind of charge-state dependence to the annihilation of trapped positrons. In order to study the influence of the paramagnetic effect only, we have made calculations for ideal vacancies.

The electron and positron structures are calculated as follows. The valence electron densities are calculated self-consistently within the density functional theory using the pseudopotential–plane-wave (PPW) scheme. In practice, the host atoms are described by norm-conserving pseudopotentials [14] and the coefficients of the plane-wave expansions are found by the steepest-descent method. This method gives the pseudo valence electron density and the corresponding Coulomb potential. The total electron density and Coulomb potential are then obtained by adding the core contribution using the free atom cores. The correlation part of the positron potential is calculated within the LDA using the interpolation formula by Boroński and Nieminen [15]. The pseudo valence electron density does not give the correct behaviour near the nuclei because the pseudo wavefunctions do not have nodes. This error is, however, rather small, because the total electron density is dominated in this region by the core electrons. Moreover, because the positron potential is dominated there by the Coulomb repulsion due to the nucleus, the probability of finding a positron in the core region is negligible. The positron wavefunction and eigenenergies are solved by the numerical relaxation technique [16] on a discretized mesh, which is also used for the integration of the positron annihilation rates. For comparison, and also in order to be able to cover a wider range of vacancies, we have also performed calculations using the

linear-muffin-tin-orbital method in the atomic sphere approximation (LMTO–ASA), together with Green function techniques [12,17].

In order to calculate the positron annihilation rates and the corresponding lifetimes at paramagnetic defects, the ordinary LDA expression for the annihilation rates has to be generalized along the lines described above. We assume that the enhancement of the electron density at the positron can be described by LDA. This means that at a given point r it depends only on the total electron density $n_-(r)$, which we write in the general case as

$$n_-(r) = n_c(r) + \Delta n(r) \tag{1}$$

where $n_c(r)$ is the spin-compensated and $\Delta n(r)$ the unpaired electron density.

The two-gamma positron annihilation occurs with electrons which are in a singlet state with respect to the positron spin. The density of these singlet electrons, $n_s(r)$, for a *spin-compensated* system is $n_-(r)/4$ because the probability of the singlet state is 1/4 (for the singlet state the magnetic quantum number $m_s = 0$, only, whereas $m_s = 0, \pm 1$ for the triplet state). Therefore the annihilation rate is

$$\lambda_{\mathrm{LDA}} = 4\pi r_0^2 c \int \mathrm{d}r\, n_+(r) n_s(r) \gamma(n_-(r)) = \pi r_0^2 c \int \mathrm{d}r\, n_+(r) n_-(r) \gamma(n_-(r)). \tag{2}$$

Above, $n_+(r)$ is the positron density and $\gamma(n_-(r))$ is the Boroński–Nieminen [15] enhancement factor, which is generalized for semiconductors with imperfect screening by using the high-frequency dielectric constant [10,18]. r_0 is the classical electron radius and c is the speed of light. The subscript LDA means that this is the conventional equation used in the LDA-positron-lifetime calculations.

Let us now consider a paramagnetic vacancy. For the *ortho* spin state at the defect $n_s(r) = n_c(r)/4$. The annihilation rate is thus

$$\lambda^{\mathrm{T}} = \pi r_0^2 c \int \mathrm{d}r\, n_+(r) n_c(r) \gamma(n_-(r)) \tag{3}$$

(the three-gamma annihilation for the ortho state has a very small rate, and need not be considered here). For the *para* spin state at the vacancy, $n_s(r) = n_c(r)/4 + \Delta n(r)$ and the annihilation rate is

$$\lambda^{\mathrm{S}} = \pi r_0^2 c \int \mathrm{d}r\, n_+(r)[n_c(r) + 4\Delta n(r)]\gamma(n_-(r)). \tag{4}$$

By defining the spin polarization as

$$\zeta(r) = \frac{|n_\uparrow(r) - n_\downarrow(r)|}{n_-(r)} \tag{5}$$

where $n_{\uparrow(\downarrow)}(r)$ is the density of electrons having spin up (down) the above annihilation rates assume more symmetrical forms

$$\lambda^{\mathrm{T}} = \pi r_0^2 c \int \mathrm{d}r\, n_+(r) n_-(r) \gamma(n_-(r))(1 - \zeta(r)) \tag{6}$$

for the ortho state and

$$\lambda^{\mathrm{S}} = \pi r_0^2 c \int \mathrm{d}r\, n_+(r) n_-(r) \gamma(n_-(r))(1 + 3\zeta(r)) \tag{7}$$

for the para state.

In order to estimate the magnitude of the paramagnetic effect we have performed calculations for vacancies in Si and GaAs. The main test case was the singly negative Si vacancy, V_{Si}^{-}. It has three electrons in the deep levels, one of which is unpaired. We first performed the electronic structure calculation for the ideal V_{Si}^{-} using the experimental lattice constant of 5.43 Åand a 10 Ryd cutoff in the plane wave expansion. The Bachelet–Hamann–Schlüter norm-conserving pseudopotential [14] with s-non-locality was used, the non-local part being treated by the Kleinman–Bylander procedure [19]. A simple cubic supercell with 63 atoms was used, and in the Brillouin zone sampling we used only the Γ point. For the ideal vacancy the highest-energy level is triply degenerate. We occupy each of the three spatially different gap states with one electron (Hund's rule). If the atoms are allowed to relax, the Jahn–Teller effect lowers the symmetry and splits the degenerate states.

Figure 1 represents the electron density corresponding to the highest state of the ideal V_{Si}^{-} calculated in this work. The state contains one electron and is considered as the unpaired electron for the paramagnetic effect. The wavefunction is mainly localized between two atoms neighbouring the vacancy, and it is antibonding in nature. This symmetry is in agreement with a simple LCAO picture [20]. It is interesting that we have obtained this symmetry, which is lower than expected for the ideal vacancy. The origin of the symmetry lowering has to be in the direct electron–electron interactions. The electron density in figure 1 is also in good agreement with the recent high-precision calculation of Sugino and Oshiyama [21] for the relaxed V_{Si}^{-}. Presumably due to the larger supercell (216 atoms) and relaxation, their value of the maximum density, $0.011a_0^{-3}$, is somewhat larger than our value of $0.0084a_0^{-3}$. The contribution of the unpaired electron density to the total electron density is (at maximum) about 17%. According to our calculations the position of the highest occupied level is 0.7 eV above the bulk valence band maximum, again in good agreement with the result of Sugino and Oshiyama [21]

The neutral As vacancy in GaAs (V_{As}^{0}) has one electron in the gap state and is therefore also a paramagnetic defect. According to the LCAO picture [20] the wavefunction of the unpaired electron is of bonding type within two pairs of atoms neighbouring the vacancy, and antibonding between these pairs. It is therefore very interesting to compare the results for the paramagnetic effect in this case to those for V_{Si}^{-} with a different symmetry of the unpaired electron wavefunction. The different symmetry could lead to a different strength of the paramagnetic effect. Unfortunately, according to Laasonen *et al* [5] the wavefunction of the highest state for a relaxed V_{As}^{0} is very delocalized. This can be interpreted as a sign that the highest state is actually at the conduction band. Therefore we have calculated V_{As}^{0} with the LMTO–ASA Green function method, which enables the use of the so-called scissors operator [22] opening the band gap to the experimental value. The highest occupied state of V_{As}^{0} is then in the band gap and is well localized. The drawback of LMTO–ASA is that all the densities and potentials are spherically symmetric in the atomic and tetrahedral interstitial spheres. Although the LDA lifetimes seem to be quite insensitive to ASA (see below) the symmetrization may influence the paramagnetic effect.

The positron density in V_{Si}^{-} is shown in figure 2. The positron is well localized at the vacancy and the shape of the wavefunction is similar to that in the neutral As and Ga vacancies in GaAs (see [6]).

We can now calculate the positron annihilation rates using the equations and densities mentioned above. The corresponding lifetimes for the different vacancies are given in table 1. For comparison, we also show the lifetimes for the perfect bulk Si and for some non-

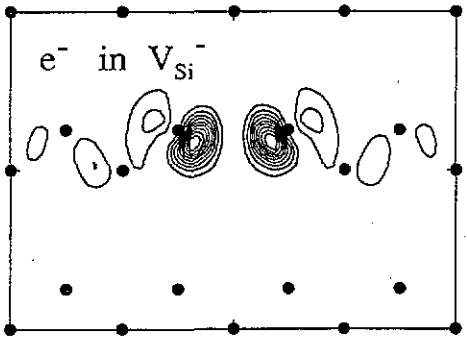

Figure 1. Electron density corresponding to the highest energy state of V_{Si}^-. The figure shows a region of the (110) plane limited by the borders of the simulation cell. The contour spacing is one tenth of the maximum value, 8.4×10^{-3} au. The Si atoms are marked by black dots.

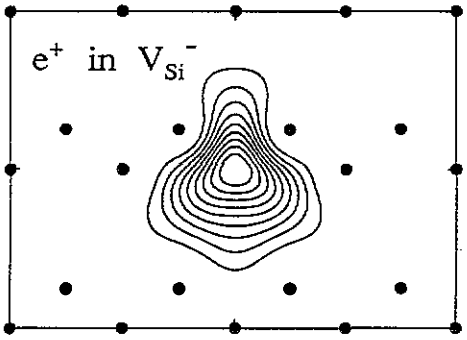

Figure 2. Positron density for an ideal V_{Si}^-. The figure shows a region of the (110) plane limited by the boundaries of the supercell. The contour spacing is one tenth of the maximum value.

paramagnetic vacancies calculated with the same methods. Within the LDA, the PPW scheme and the LMTO–ASA Green function method give nearly identical results. The slight increase of the positron lifetime when the vacancies become more negative is due to the increase of the localization of the positron wavefunction to the vacancy.

Table 1. Positron lifetimes (in ps) for bulk Si and for different vacancies in Si and GaAs calculated with the pseudopotential–plane-wave (PPW) and LMTO–ASA Green function (LMTO) methods.

	PPW			LMTO		
	LDA	ortho	para	LDA	ortho	para
Bulk Si	218	—	—	219	—	—
V_{Si}^-	252	258	238	251	258	231
V_{Si}^{2-}	254	—	—	252	—	—
V_{As}^0	—	—	—	259	266	240
V_{As}^-	—	—	—	262	—	—
V_{Ga}^{2-}	—	—	—	261	266	246
V_{Ga}^{3-}	—	—	—	262	—	—

For the ideal vacancies in table 1, the ortho–para splitting of the lifetime is seen to be at least 20 ps. The maximum splitting of 27 ps is found by the LMTO–ASA Green function method in the case of V_{Si}^-. The ortho lifetimes are 5–7 ps longer than the LDA lifetimes. The LMTO–ASA Green function method gives a larger splitting in the case of V_{Si}^-. The difference in the ortho–para splitting reflects the different overlaps of the electron and positron densities in the two methods of calculation.

The ortho, para, and LDA lifetimes for V_{Si}^- are given in figure 3 as a function of the positron–electron overlap defined as

$$O = \int \mathrm{d}r\, n_+(r) n_-(r). \tag{8}$$

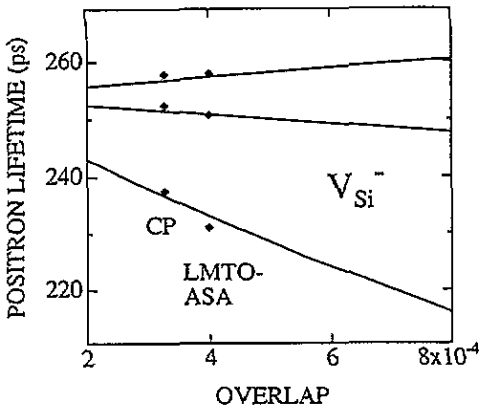

Figure 3. Positron lifetime components for the negative vacancy in Si as a function of the overlap of the electron and positron densities. The points are the results of the Car–Parrinello and LMTO–ASA Green function calculations, the curves are obtained by using a spherical model with box potentials for positron and unpaired electron.

The full curves are obtained by using a spherical model in which the unpaired electron and positron wavefunctions correspond to box potentials [23] and the overlap is controlled by varying the electron or positron potential parameters. In this spherical model the compensated electron density is a constant chosen so that the results agree as well as possible with those from the PPW and LMTO–ASA Green function schemes. It can be seen that the difference in the ortho–para splitting between the PPW and LMTO–ASA Green function methods can be understood to result from different values of overlaps. The splitting depends strongly on the overlap. Because the electron wavefunction is much more delocalized than the positron wavefunction, the overlap can be most easily increased by increasing the degree of localization of the electron wavefunction. Therefore, the paramagnetic effect should be largest for vacancies, in which the paramagnetic electron wavefunction is well localized. According to recent first-principles calculations one such case should be the neutral phosphorous vacancy in InP [24].

The experimental verification of the paramagnetic effect by lifetime measurements may be difficult in many cases. A two-component fit is usually made in analyzing the lifetime spectra [7]:

$$\tau = I_1\tau_1 + I_2\tau_2 \tag{9}$$

where τ_1 is determined by the positron bulk annihilation rate λ_{bulk} and the trapping rate κ to defects:

$$\tau_1 = 1/\lambda_{bulk} + 1/\kappa. \tag{10}$$

τ_2 is the lifetime related to trapped positrons. I_1 and I_2 are the corresponding intensities. If the difference between the ortho and para lifetime components is so large that the para lifetime component is close to τ_1, τ_2 is purely the ortho lifetime component. In a typical case, this requires that the para lifetime component should be much shorter than the positron bulk lifetime because of the trapping rate contribution to τ_1. Then I_2 should saturate to 75%, which could be used as evidence for the paramagnetic effect. If the splitting is small, the ortho and para lifetime components both contribute to τ_2. The theoretical counterpart of τ_2 is in this case the spin-averaged or LDA lifetime and the existence of the effect cannot be demonstrated. It could possibly be used in the measurements samples for which the positron trapping to vacancies is saturated. In this case the two-component analysis gives directly the ortho and para lifetime components provided that their splitting is large enough to be detected with finite experimental statistics.

According to table 1 the para lifetime components estimated for V_{Si}^{-} and V_{As}^{0} are longer than the positron bulk lifetimes. Thus, it is expected that the para and ortho components are mixed when the trapping into vacancies is unsaturated. The splitting of the ortho and para lifetime components is so small that in the case of saturated trapping their decomposition with statistics typical in lifetime measurements is hardly possible. The splitting depends strongly, however, on the overlap of the electron and positron wavefunctions as seen in figure 3. In particular, the electron wavefunction may be influenced by different approximations in the calculation method and therefore our results obtained by the PPW scheme and the LMTO–ASA Green function method should be considered as order of magnitude estimates. The important result is, in figure 3, the dependence of the different lifetimes and ortho–para splitting on the overlap, which turns out to be the relevant parameter determining the strength of the paramagnetic effect.

As can be seen also from table 1, the positron lifetimes calculated in the LDA scheme for the ideal vacancies do not depend strongly on the charge state. On the other hand, the measurements for As vacancies in GaAs [4] and phosphorous–vacancy pairs in Si [3] show large positron lifetime changes between different charge states. The discrepancy has been explained by arguing that the atomic relaxation depends strongly on the charge state [6,13]. It is tempting to think that the paramagnetic effect could also contribute to the large experimental positron lifetime changes. This means that the longer lifetimes correspond to the ortho components for the paramagnetic defects and the shorter lifetimes are seen when the defects are spin-compensated and the LDA scheme for the annihilation is valid. Indeed, the longer lifetime seen for the As vacancy and that for the phosphorous–vacancy pair are connected [3,4] with the neutral states, which are paramagnetic. The shorter lifetimes are connected with spin-compensated negative states in both cases. However, as discussed above, the estimated splittings of the ortho and para lifetimes in table 1 are not large enough to convincingly rule out the LDA estimate of the longer lifetime.

Magnetic quenching [7] in two-dimensional angular correlation (2D-ACAR) experiments could be a way to see the paramagnetic electron effect. In a high magnetic field the ortho and para $m_S = 0$ states are mixed and the two-gamma annihilation increases. This results in an increase of the annihilation rate in the region of small positron–electron momentum relative to annihilation at the high momentum region. This change is less ambiguous than the consequences of the paramagnetic effect in the lifetime spectroscopy. Moreover, the change in the ACAR spectrum is proportional to the Fourier transform of the wavefunction of the unpaired electron and thereby the spatial distribution of the unpaired electron could be probed directly. Therefore this kind of measurements could complement the information obtained by electron paramagnetic resonance [11]. As a matter of fact, magnetic quenching-2D-ACAR experiments for V_{As}^{0} are already in progress [25] but no conclusive results have been obtained yet.

In conclusion, we have studied the paramagnetic effect that should be considered in the context of positron annihilation at defects in semiconductors. The effect occurs for defects having an odd number of electrons at deep levels. It splits the positron defect lifetime at the defect into two components. However, according to our quantitative estimates the effect is difficult to detect in the positron lifetime measurements for the vacancies in Si and in GaAs and cannot be extracted from the charge-state induced positron lifetime changes for these vacancies. However, in defects with more strongly localized deep electron wavefunctions the effect becomes more important and should be taken into account. Prime canditates for such systems include vacancies in II–VI compound semiconductors. Finally, we suggest magnetic quenching-2D-ACAR experiments in order to investigate the effect more directly.

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