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Annihilation of delocalized positrons: a comparison of diamond and silicon

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Abstract

We present *ab initio* pseudopotential calculations on the lifetime and electron–positron momentum density of delocalized positrons in bulk diamond and silicon. Our results compare very well with experimental and earlier theoretical findings available. For diamond we observe a comparatively isotropic momentum distribution with maximum density at the Γ point which explains naturally recent experimental results.

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1. Introduction

Experimental techniques based on positron annihilation have become an increasingly important tool for probing the electronic and atomic structure of solids. Three-dimensional electron–positron momentum distributions can now be obtained from the angular correlation of annihilation radiation (ACAR). ACAR measurements for a series of semiconductors (Si, Ge, GaAs, InP and GaSb) [1,2] show a strong anisotropy accompanied by the appearance of a deep dip around the Γ point in the electron–positron momentum distributions for the elemental semiconductors. These features were found to be less pronounced for the III–V compounds. This different behaviour has been traced

back to the reduced symmetry of the compound semiconductors. The symmetry lowering from O_h to T_d revives some bands which are annihilation inactive in case of elemental semiconductors [1,3]. However, the ACAR spectrum for diamond shows an even stronger reduction of the anisotropy and the disappearance of the dip around the origin in k -space [1,2]. These differences to the elemental semiconductors Si and Ge obviously cannot be explained by symmetry considerations. Therefore it has been speculated that they are due to a large number of defects in the examined diamond sample [1]. On the other hand, recent *first principles* calculations [4] explain the differences between diamond and other group-IV semiconductors in terms of the small diamond lattice constant and the weak electron–positron correlation effects in diamond. The aim of our study is to contribute to a better understanding of the annihilation characteristics of delocalized positrons in diamond and silicon.

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2. Method

Our calculations are based on two-component density-functional theory (DFT) [5,6], a generalization of the one-component DFT that represents each species of particle by a distinct density. Assuming a delocalized positron wave function, the positron density is negligible at every point of the infinite lattice and the electronic structure of the host remains unaltered. Therefore it is sufficient to constrain self-consistency to the calculation of the electron ground state in the absence of positrons. Our electronic ground state calculation rests on the local-density approximation (LDA) for the description of many-body electron–electron interaction. The electron–ion interaction is accounted for by using fully separable, norm-conserving pseudopotentials [7] and is limited to a consideration of the valence electron density. The carbon pseudopotential has been softened [8] to yield fully converged results already with a relatively low energy cutoff of 42 Ryd for the plane wave basis set. For silicon 20 Ryd are taken. The same cutoff energies were used for both the electron and positron wavefunctions. The k -space integration is replaced by a sum over four special points in the irreducible part of the Brillouin zone. The minimum of the total-energy functional with respect to the electronic degrees of freedom is found by employing a molecular-dynamical approach [9]. We use the experimental lattice constants in our calculation.

The potential sensed by the positron is calculated from the sum of the self-consistently calculated Coulomb potential V_C and the electron–positron correlation potential V_{corr} in LDA,

$$V_{\text{eff}}(\mathbf{r}) = V_C(\mathbf{r}) + V_{\text{corr}}(n(\mathbf{r})). \quad (1)$$

V_C consists of the local part of the crystal pseudopotential used for electrons, plus the Coulomb potential due to the valence electron charge distribution. For the correlation potential we take the expression

$$V_{\text{corr}}(n(\mathbf{r})) = V_{\text{corr}}^{\text{EG}}(n(\mathbf{r})) \sqrt[3]{f(n, \epsilon_g)}, \quad (2)$$

where $V_{\text{corr}}^{\text{EG}}$ is the zero-positron-density limit of the electron–positron correlation potential. It equals the correlation energy for a delocalized positron in a homogeneous electron gas. We use the parametrization by Boroński and Nieminen [10]. This expression

works well in case of (simple) metals, but in semiconductors such as diamond or silicon the existence of the band gap reduces the screening [6]. In order to take the reduced screening into account the correlation potential is scaled with a factor $\sqrt[3]{f}$, where

$$f(n, \epsilon_g) = 1 - \frac{0.37\epsilon_g}{1 + 0.18r_s}, \quad r_s = \sqrt[3]{\frac{3}{4\pi n}} \quad (3)$$

with $\epsilon_g = 2$ [5,11]. The positron wave function $\psi_0^+(\mathbf{r})$ is then obtained by diagonalizing the corresponding Schrödinger equation in k -space using the same energy cutoff as for the electronic wave functions. We are only interested in the lowest energy state with the positron momentum $\mathbf{p} = 0$. Our approach is similar to two recent calculations by Puska et al. [12] and Panda et al. [4]. In these works the positron–ion core interactions is treated by means of frozen core densities of free atoms: An attractive potential due to the core electrons plus a repulsive Coulomb potential due to the nucleus have been considered. In contrast to that we describe the positron–ion core interaction by the same pseudopotential technique applied to the electron–ion interaction. This leads to a complete neglect of the positron annihilation with core electrons and allows only an approximate description of the positron wavefunction near the nucleus. This should, however, only very little impair the accuracy of our results, because the positron avoids the core region.

3. Results

3.1. Lifetime

The total positron annihilation rate can be determined from the overlap of the positron and electron density. The calculated ground state density for a delocalized positron in diamond can be seen in Fig. 1. The positron is mainly localized in the interstitial region and the probability is essentially zero around the nuclei due to the repulsive potential from the core charge. The maximum probability is located at the tetrahedral site, which is farthest from the nearest atomic positions. We find the shape of the positron density in silicon qualitatively very similar to diamond. The calculated densities resemble closely the results of Refs. [3,13].

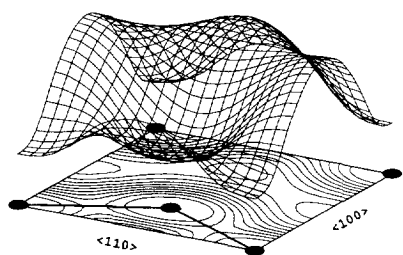


Fig. 1. Three-dimensional perspective view and contour plot of the squared ground state wave function of a delocalized positron in diamond in the (110) plane. Contours are spaced by $0.001 \text{ e} \times \text{Bohr}^{-3}$.

Once the electron and positron densities are given, one has to account for the enhanced annihilation rate caused by attractive correlation of electron and positron. Thus, in LDA the annihilation rate λ reads [10]

$$\lambda = \pi r_0^2 c \int d\mathbf{r} n^+(\mathbf{r}) n^-(\mathbf{r}) g(0; n^+, n^-) \quad (4)$$

Here r_0 and c are the classical electron radius and the speed of light, respectively. Since we are considering a delocalized positron in the infinite lattice, the low positron density limit of the pair correlation function at the origin g has to be taken. For $g(0; n^- \rightarrow 0, n^-)$ we use the parametrization of Ref. [10]. In Eq. (4) it is assumed that the positron is completely screened by electrons. This is certainly not the case for diamond or silicon, therefore we give also results for the annihilation rate calculated using a modified g which takes the reduced screening into account [14]. The positron lifetime is given by $\tau = 1/\lambda$.

Our calculated bulk positron lifetime in diamond amounts to 93 ps. When we account for the reduced screening in the expression for g according to Ref. [14] a slight increase of the lifetime to 96 ps occurs. This is still somewhat smaller than the experimental values of 110–115 ps [15], but is in near perfect agreement with another recent measurement, by Li and co-workers [16], who determined a lifetime of 97.5 ± 1.5 ps. The complete neglect of positron annihilation with core electrons in the present study leads to a lifetime overestimation by about 1% according to Ref. [17]. Therefore it cannot explain the slight lifetime underestimation in our calculation. Apart from obvious experimental uncertainties the deviation may be due to the

large band gap in diamond. It makes the description in the picture of a homogeneous two-component plasma used as starting point to model the electron–positron correlation (Eq. (2)) and the electron enhancement at the positron site (Eq. (4)) questionable. However, the correction of these formulae for the reduced screening partly lifts this discrepancy. It turns out that the modification of the correlation potential (Eq. (3)) is of minor importance for the calculation of λ . It prolongs the lifetime by less than 0.1%. Earlier theoretical approaches also determined the lifetime for delocalized positrons in diamond somewhat shorter than experiment. Starting from superimposed atomic charge densities Puska et al. calculate 92 ps [13] and 83 ps [17].

For silicon we arrive at a positron lifetime of 220 ps. If the reduced screening is accounted for in the enhancement [14], the lifetime prolongs to 228 ps. The latter value is somewhat larger than the experimental findings of 218–222 ps [18]. However, this overestimation can be explained by the neglect of the positron annihilation with the core electrons, which amounts to about 2.2% of the total annihilation rate in case of Si [17]. Earlier theoretical results for the bulk positron lifetime are 220 ps from a linear-muffin-tin-orbital (LMTO) band-structure method [11] and 219 ps from a calculation based on the superposition of atomic charge densities [17,19].

The positron lifetimes in diamond and silicon differ by a relatively large amount, which can simply be explained by the higher valence electron density in diamond. However, also the annihilation process itself occurs somewhat differently for the two materials. According to Eq. (4) the product: $n^+(\mathbf{r}) n^-(\mathbf{r}) g(0; n^+, n^-)$ describes the local distribution of the annihilation. In case of diamond this product assumes its maximum in the bond center. There it is nearly twice as large as in the interstitial region. For silicon we obtain a different picture: The local variation of the density product is much smaller and we find the maximum shifted away from the bond center towards the interstitial region. This different behaviour is mainly due to the positron density, which in case of diamond is slightly higher in the bond center compared with silicon.

3.2. Momentum distribution

Within an independent particle approximation the momentum distribution of the annihilating electron–positron pairs in the perfect crystal lattice can be written as [6]

$$\rho(\mathbf{P}) = 2 \sum_{n,k} f(n, \mathbf{k}) \times \left| \int_{\Omega} d\mathbf{r} e^{-i\mathbf{P} \cdot \mathbf{r}} \psi_0^+(\mathbf{r}) \psi_{n,k}^-(\mathbf{r}) \right|^2 \delta_{\mathbf{P}, \mathbf{k}+\mathbf{G}}, \quad (5)$$

where $f(n, \mathbf{k})$ is the Fermi function, $\psi_{n,k}^-(\mathbf{r})$ is the electron Bloch state with band index n and wave vector $\mathbf{k}$, Ω is the volume of the primitive cell and $\mathbf{G}$ denotes a reciprocal-lattice vector.

In Fig. 2 the calculated electron–positron momentum distribution for diamond is shown. We find a relatively small anisotropy in the (100) plane compared to the results for the (110) plane. In the latter case we observe a much stronger confinement of the momentum distribution in [110] direction than along [100]. This agrees very well with the momentum distribution measured by Liu and co-workers [2]. The electron–positron momentum distribution for silicon in the (100) and (111) plane are shown in Fig. 3. In Fig. 3a two characteristics are striking: (i) a dip appears around the Γ point which runs into a valley parallel to [100] and (ii) the maximum of the momentum distribution is assumed on the [110] direction which appears as a ridge. These features have also been found experimentally [1] and described theoretically [3,4]. In particular, the ratio of the annihilation rate between the maximum and Γ points are reported to be 1.19 (experiment [1]) and 1.03 (theory [3]). We calculate a value of 1.04 for this ratio. When comparing our results for the momentum distribution with experiment, a word of caution is in order. The calculations are based on pseudopotential theory. Apart from the complete neglect of the core electrons also the pseudo-wave functions describing the valence electrons are accurate only outside the core region. These functions have no nodes and vary moderately within the core region, where the real wave functions oscillate rapidly. Although the very low amplitude of the positron wave function around the nuclei may weaken the effect, we still expect an underestimation of the

calculated distribution in the region of high momentum which may contribute to the deviation mentioned above. Considerable anisotropy is also found in the (110) plane (cf. Fig. 3b). Here we find a valley along the [111] direction. Such a valley has also been found experimentally for Ge [2].

Comparing the electron–positron momentum distributions of diamond (Fig. 2) and silicon (Fig. 3) we find pronounced differences. In particular the dip at the Γ point and the valleys along [100] and [111] observed for silicon essentially disappear for diamond. This is in agreement with experiment [1], but has been attributed to a large number of defects in the diamond sample. Our results show that these diamond peculiarities will be observed also for perfect crystals. In order to understand the observed differences between the two systems and to investigate the influence of the positron wave function on the momentum distribution we have performed calculations assuming the positron wave function to be constant throughout the crystal. We find that the main effect of the actual positron density is a rather uniform contraction of the momentum distribution along all directions. This explains why the assumption of a constant positron wave function has proved to work rather well for carbon bonds [20]. In Ref. [3] it has been shown that the momentum distribution of the electrons in the two upper valence bands of Si and GaAs gives rise to the valleys and the dip observed in the ACAR spectra for these materials. Looking at the annihilation contribution from the different electronic bands we find that in particular these more p-like states (see, e.g., Ref. [21]) give rise to a much more isotropic momentum distribution in case of diamond compared to silicon. This is in agreement with the analysis given by Panda et al. [4] for group-IV semiconductors. They also stress the importance of the weaker electron–positron correlation effects in diamond compared to silicon. We find, however, that the main differences between diamond and silicon with respect to the annihilation characteristics are already present in the bare electronic structure of these materials.

4. Summary

We have performed ab initio pseudopotential calculations for delocalized positrons in diamond and sili-

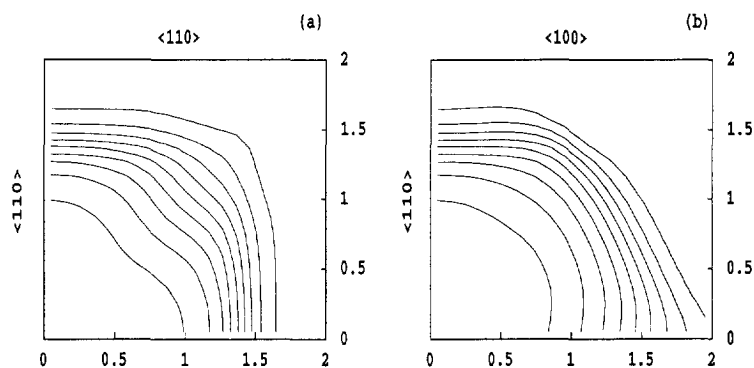


Fig. 2. Three-dimensional electron-positron momentum distribution for diamond in (a) the $\langle 100 \rangle$ plane and (b) the $\langle 110 \rangle$ plane, respectively. The contour spacing is $\frac{1}{10}$ of the maximum value. Units of the position in the momentum space are $2\pi/a$ with a being the lattice constant.

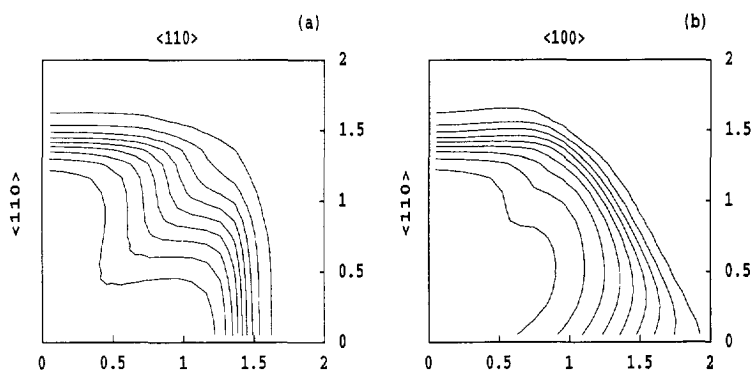


Fig. 3. Three-dimensional electron-positron momentum distribution for silicon on (a) the $\langle 100 \rangle$ plane and (b) the $\langle 110 \rangle$ plane, respectively. The contour spacing is $\frac{1}{10}$ of the maximum value. Units of the position in the momentum space are $2\pi/a$ with a being the lattice constant.

con. The results for the positron lifetimes are in close agreement with experiment. The remaining slight differences in case of diamond reflect most probably the difficult description of correlation effects in wide-band gap materials. However, there is also an appreciable scatter in the experimental results. We find remarkable differences in the electron-positron momentum distribution between Si and C. These differences can be traced back to the intrinsic electronic structure of the bulk materials and give a natural explanation for the outcome of recent ACAR experiments.

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References

- [1] S. Tanigawa, *Hyperfine Interact.* 79 (1993) 575.
- [2] W. Liu, S. Berko and A.P. Mills Jr., *Mat. Sci. Forum* 105–110 (1992) 743.

- [3] M. Saito, A. Oshiyama and S. Tanigawa, *Phys. Rev. B* 44 (1991) 10601.
- [4] B.K. Panda, S. Fung and C.D. Beling, *Phys. Rev. B* 53 (1996) 1251.
- [5] M.J. Puska, *Phys. Status Solidi (a)* 102 (1987) 11.
- [6] M.J. Puska and R.M. Nieminen, *Rev. Mod. Phys.* 66 (1994) 841.
- [7] X. Gonze, R. Stumpf and M. Scheffler, *Phys. Rev. B* 44 (1991) 8503.
- [8] B. Wenzien, P. Käckell and F. Bechstedt, *Surf. Sci.* 307–309 (1994) 989.
- [9] R. Car and M. Parrinello, *Phys. Rev. Lett.* 55 (1985) 2471; R. Stumpf and M. Scheffler, *Comput. Phys. Commun.* 79 (1994) 447.
- [10] E. Boronński and R.M. Nieminen, *Phys. Rev. B* 34 (1986) 3820.
- [11] M.J. Puska, O. Jepsen, O. Gunnarson and R.M. Nieminen, *Phys. Rev. B* 34 (1986) 2695.
- [12] M.J. Puska, A.R. Seitsonen and R.M. Nieminen, *Phys. Rev. B* 52 (1995) 10947.
- [13] M.J. Puska and R.M. Nieminen, *J. Phys. Condens. Matter* 4 (1992) L149.
- [14] M.J. Puska, *J. Phys. Condens. Matter* 3 (1991) 3455.
- [15] H.-E. Schaefer, M. Forster, R. Würschum, W. Krätschmer and D.R. Huffman, *Phys. Rev. B* 45 (1992) 12164; R. Suzuki, Y. Kobayashi, T. Mikado, H. Ohgaki, M. Chiwaki, T. Yamazaki, A. Uendono, S. Tanigawa and H. Funamoto, *Japan. J. Appl. Phys.* 31 (1992) 2237; S. Dannefaer, *J. Phys. C* 15 (1982) 599.
- [16] X.-S. Li, S. Berko and A.P. Mills Jr., *Mat. Sci. Forum* 105–110 (1992) 739.
- [17] M.J. Puska, S. Mäkinen, M. Manninen and R.M. Nieminen, *Phys. Rev. B* 39 (1989) 7666.
- [18] W. Fuhs, V. Holzhauser, S. Mantl, F.W. Richter and R. Sturm, *Phys. Status Solidi (b)* 89 (1978) 69; S. Dannefaer, P. Mascher and D. Kerr, *Phys. Rev. Lett.* 56 (1986) 2195; G. Dlubek and O. Brünner, *Ann. Phys. (Leipzig)* 7 (1986) 178.
- [19] M.J. Puska and C. Corbel, *Phys. Rev. B* 38 (1988) 9874.
- [20] S.Y. Chuang and B. G. Hogg, *Can. J. Phys.* 45 (1967) 3895.
- [21] J.P. Walter and M.L. Cohen, *Phys. Rev. B* 4 (1971) 1877.