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First-principles calculation of positron lifetimes in solids

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We present a first-principles approach for calculating the positron lifetime in metals. Convenient expressions are provided for the electron-positron correlation function and the enhancement factor. Calculations on a wide range of elemental metals and some monovacancies are found to be in excellent agreement with experiment. The approximations inherent in this approach and the treatment of the core-electron contribution are discussed.

I. INTRODUCTION

Positron annihilation provides a sensitive probe of defects in materials, since the positrons often annihilate preferentially at defect or vacancy sites.[1] One of the outstanding problems in the area is the characterization of these defects based on positron-lifetime measurements. Typically, the experimentally measured lifetime may give some evidence for the presence of defect trapping, such as a temperature dependence in the lifetime spectrum, but it is very difficult to correlate this with a specific defect or set of defects. In other cases, although the spectrum may be temperature independent, it may still be dominated by the defect structure, with almost all of the annihilations due to positrons in trapped states in the material. As a consequence, this lifetime could be misinterpreted as a bulk, defect-free lifetime. Many of these problems of interpretation could be resolved with theoretical calculations of the expected lifetimes for the bulk material and associated defects. In the past, most attempts to calculate the lifetime have been based either on parametrized fits to experimental data,[2,3] assuming that the samples were sufficiently defect-free in some limit where the bulk-annihilation rate could be fitted, or on calculations using nonoverlapping atomic charge densities which take no account of charge rearrangement in the solid or in the vicinity of a defect.[4] There have been few attempts to calculate lifetimes from first principles for self-consistent charge densities, and these have been confined to free-electron-like metals.[5]

In this paper, we present calculations of positron lifetimes in metals based on first-principles electronic-structure calculations for both the electrons and positrons. The electron and positron many-body interactions are computed using a density functional approach where the parameters are derived from free-electron gas calculations. In contrast to previous approaches, we not only avoid a parametrized fit to positron-lifetime experiments[3] but also use a more realistic self-consistent (as opposed to superimposed atom[4]) electron charge density in the calculation. The calculated bulk lifetimes are in excellent agreement with experiment for a wide variety of elemental metals, including free-electron materials, transition metals, and rare earths. Similarly good agreement is found for vacancies and metallic alloys. These calculations serve to demonstrate the reliability of this theoretical approach.

II. METHOD

When a positron enters a solid, it thermalizes rapidly and is either trapped in a defect in an imperfect crystal, or enters a low-momentum Bloch state in a periodic system. The positron subsequently annihilates with an electron, and the emitted annihilation radiation is observed. The positron-annihilation rate λ, the inverse of the lifetime τ, is given by the equation[6,7]

$$\lambda = 1/\tau = \frac{\pi r_0^2 c}{e^2} \int d^3\mathbf{r}\, n^+(\mathbf{r}) n(\mathbf{r}) \Gamma(n(\mathbf{r})) \, , \tag{1}$$

where r_0 is the classical electron radius, n is the ground-state electron charge density, n^+ is the positron charge density, and Γ is an enhancement factor which takes account of the fact that the electrons are attracted towards the positively charged positron, so increasing the overlap and hence the annihilation rate. The calculation of the lifetime then involves three distinct steps. First, the self-consistent electron charge density is determined, then the positron charge density is calculated, and finally the integral in Eq. (1) is performed to yield the annihilation rate.

The electron charge density is found by performing a self-consistent electronic-structure calculation for the material. We use the linear-muffin-tin-orbital (LMTO) method with the atomic-sphere approximation (ASA) for this step.[8] Electron-electron interactions are treated in the usual way through the local density approximation (LDA) to density functional theory,[9] using the von Barth–Hedin form of exchange-correlation potential.[10] The calculations presented here are all-electron calculations, so both the core and valence electrons are taken to self-consistency in determining the ground-state charge density. The differences between the all-electron and frozen-core calculations are generally small for the systems we consider.

The positron has relaxed into its lowest available energy state by the time it annihilates, so variational methods can be employed to determine the positron wave function and hence n^+. The positron calculations are carried out using the LMTO method in exactly the same way as the corresponding electron calculations. We assume that the positron wave function is periodic and perform the calculation at the Γ point to find the lowest-energy positron state. The positron Schrödinger equation,

$$[-\tfrac{1}{2}\nabla^2 - V_{\text{ion}}(\mathbf{r}) - V_{\text{Hartree}}(\mathbf{r}) + V_{e^-e^+\,\text{corr}}(n(\mathbf{r}))]\psi^+ = E^+\psi^+ , \qquad (2)$$

consists of the kinetic-energy term, the Coulomb interaction with the ions V_{ion}, the interaction with the electron charge density V_{Hartree}, and an electron-positron correlation term $V_{e^-e^+\,\text{corr}}$. The ionic and Hartree terms are identical to those used in the electronic calculation, except for a change in sign due to the positive charge on the positron, and the Hartree term is determined directly from the self-consistent electron charge density. We treat the electron-positron correlation term by means of a local density approximation. No assumptions are made about the symmetry of the positron wave function, although, in general, it is found to have the expected s-like symmetry.

In order to avoid errors introduced by the energy linearization in the LMTO method, we use an initial guess for the pivotal energy parameter and then iterate until the positron eigenvalue and energy parameter are equal. We initially set this parameter to the energy at which the logarithmic derivative of the positron s wave function vanishes on the atomic-sphere boundary, as expected on the basis of a Wigner-Seitz argument.[3,4] For monatomic species, this gives an excellent estimate of the positron energy, and the energy parameter generally needs no further iteration. For multiatom unit cells such as metallic alloys or the vacancy calculations, each atom will give a different estimate of the positron energy, so we use the average to determine the initial guess for the energy parameter. In general, this initial value is not a sufficiently accurate estimate of the positron energy and iterating on the energy parameter is a more accurate way of determining the positron energy. In some cases, particularly in multiatom unit-cell calculations, the energy linearization breaks down for the higher-l orbitals. This manifests itself most clearly in the calculation of unphysically low-positron energies. This problem is cured by resetting the energy parameters on the relevant orbitals to higher values. A convenient choice is the C parameter, which represents an estimate of the center of the canonical band for the given orbital.[8] The positron energy invariably converges to a physical solution when this procedure is adopted on p and higher orbitals, while the s orbitals are still set to the iteratively calculated positron energy. This procedure usually converges in no more than three iterations.

The positron charge density is required to calculate the lifetime, and this can, in principle, be computed by using a two-component density functional theory to treat the electron-positron interactions.[6,7] In practice, we must employ the same kind of approximations as are used in the application of density functional theory to the electronic-structure problem and find some approximation to the exact functional. The standard approach is to use the LDA, where the potential at a given point $\mathbf{r}$ is that which a positron would feel in a free-electron gas with the charge density $n(\mathbf{r})$. The LDA has been highly successful in calculations of electronic structure, and we expect it to be even more accurate in its application to this problem, since positrons are strongly repelled by the positively charged nucleus and so tend to occupy regions of space where the electronic charge density is very slowly varying.

The electron-positron correlation potential is obtained by fitting it to the free-electron gas calculations of Arponen and Pajanne.[11] A previous fit to this data used four different functional forms to represent this potential across the entire range of electron densities.[6] To simplify the calculations, we have obtained an accurate fit to a single functional form (in rydbergs):

$$V_{e^-e^+\,\text{corr}}(r_s) = -1.56(\arctan r_s)^{-1/2} + 0.1324\exp\left[-\frac{(r_s-4.092)^2}{51.96}\right] + 0.7207 , \qquad (3)$$

where $(4\pi/3)r_s^3 n = 1$. This fit has the correct limiting behavior at both low and high densities, but it deviates slightly from the more complicated fit[6] in the very-high-density region. Since the positron will only sample regions of relatively low charge density in solid-state applications, this difference will have a negligible effect on our results. For r_s values larger than about 1, our expression provides an excellent fit to the values calculated by Arponen and Pajanne.[11]

While the positron charge density can, in principle, be calculated exactly within density functional theory, this is not the case for the enhancement factor Γ, which is related to the polarization of the electron gas to the presence of the positron. Nevertheless, the positron samples such a flat and featureless part of the charge density that a calculation based on free-electron values is expected to give an accurate description of this response function. We have used the following expression, which is derived by fitting to the free-electron gas calculation of Lantto:[6]

$$\Gamma(r_s) = 1 + 0.1512 r_s + 2.414 r_s^{3/2} - 2.01 r_s^2 + 0.4466 r_s^{5/2} + 0.1667 r_s^3 . \qquad (4)$$

This differs only slightly from the form proposed by Boroński and Nieminen.[6]

The fits that we have presented for the electron-positron correlation energy and the enhancement factor are numerically very close to those previously presented.[6] In general, the fitted functions lie within the uncertainties of the electron-gas calculations on which they are based and are in particularly good agreement over the physically interesting charge density range of $r_s \sim 2$–6. For the electron-positron correlation function, the maximum error in our fits is only 0.07%, and Eq. (3) is significantly easier to implement than the rather complicated form proposed in Ref. 6. Our expression for the enhancement factor is a more accurate fit of the electron-positron gas data to the functional form used in Ref. 6. These different fits to the correlation energy and enhancement factor can give differences in calculated lifetimes of up to about 2 ps and so contribute a relatively minor uncertainty to the calculated lifetime, which is typically in the range of 100 ps or more. Much larger changes, of order 10 ps or more, result from the use of the empirical Brandt-Reinheimer expression.[2]

It is important to realize that while density functional theory is applicable to the calculation of the positron charge density, the use of the LDA has much less validity in the calculation of the enhancement factor Γ. This becomes particularly apparent when we consider the contribution of the core electrons to the annihilation rate. Theoretical estimates for the enhancement factor of the core electrons range from the independent particle model (IPM), value of 1 (i.e., no enhancement) to about 2.[12] Since the core electrons are much less polarizable than the valence electrons, we expect that using the same enhancement factor on the core and valence electrons together will overestimate the response of the tightly bound core electrons to the presence of the positron, and so result in a shorter lifetime. We have therefore investigated two approximations for the core- and valence-enhancement factors. The first consists of the straightforward application of Eq. (1), with the total (core plus valence) electronic charge density appearing throughout. In the second approximation, separate enhancement factors are used for the core and valence electrons. The core terms are treated within the IPM, while the valence electrons are enhanced by $\Gamma(n_{\text{val}})$ so that

$$\lambda = \frac{\pi r_0^2 c}{e^2} \int d^3\mathbf{r}\, n^+(\mathbf{r}) \{ n_{\text{core}}(\mathbf{r}) + n_{\text{val}}(\mathbf{r}) \Gamma[n_{\text{val}}(\mathbf{r})] \} \ . \qquad (5)$$

Note that in both cases $V_{e^-e^+\,\text{corr}}$ is calculated with the full electronic charge density, in keeping with the tenets of density functional theory.

III. RESULTS AND DISCUSSION

The experimental and calculated theoretical lifetimes are presented in Table I for a variety of metals and metallic monovancies. The equilibrium lattice structures and lattice constants are used for the elemental metals. The LMTO basis set consists of *s*, *p*, and *d* orbitals on each site in all cases except gadolinium, where the *f* orbitals were also included. The same basis set is used in both the electron and positron calculations. By and large, the agreement with experiment is excellent; the calculations are typically within about 5% of the experimental values for both treatments of the enhancement factor. In only a few cases does the discrepancy exceed 10%. This agreement is graphically demonstrated in Fig. 1 where we have plotted the experimental lifetime against the theoretical lifetime calculated from Eq. (5). Complete agreement with experiment would correspond to points lying on the diagonal line. Note that we cover a wide range of systems, including alkali metals, transition metals, and even the rare-earth metal gadolinium, and that the same density-dependent enhancement factor is used throughout. Note that the density dependence of the enhancement naturally leads to different enhancements on different orbitals. In contrast to earlier work,[3] we do not need to invoke separate enhancement factors for the *sp*, the *d*, and the *f* electrons. All the valence electrons, regardless of their symmetry, are treated in the same way. The results for vacancies are also in excellent agreement with experiment, confirming that the method is applicable to systems other than close-packed metals. We stress again that all of these results have been obtained with the same criterion for the electron-positron interactions, with the parameters determined by first-principles calculations on the free-electron gas and that there is no fitting to any experimental data on positron annihilation.

As a further test of the method, we considered the intermetallic alloy Ni_3Al which has a well-characterized bulk lifetime of 110 ps.[17] This is also in very good agreement with our calculations, where we find 110 ps from Eq. (5) and 105 ps from Eq. (1).

The ASA in the LTMO replaces the polyhedral unit cell with a sphere, and all integrals are carried out in the sphere rather than in the cell. This shape approximation generally has a small effect on the electrons, since they are so strongly attracted by the central potential around the atom. For the positron, however, it is possible that the discrepancies introduced by the ASA may be somewhat larger, since the positron is located in the interstitial region where the effects of the ASA are most pronounced. In order to evaluate the severity of this approximation, we replaced the atomic sphere with one muffin-tin-sized sphere around the atom and filled up the interstitial volume with one empty sphere for fcc systems and

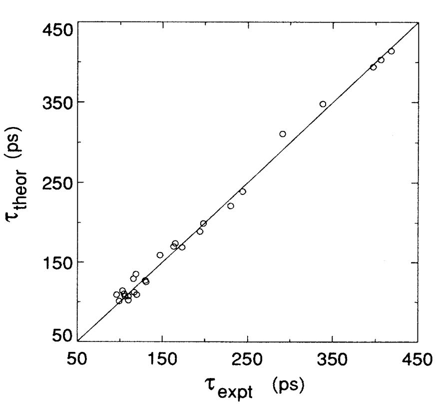

FIG. 1. Theoretical vs experimental lifetimes in ps for a variety of elemental metals, monovacancies, and metallic alloys calculated using Eq. (5). Theoretical calculations in exact agreement with experiment lie on the diagonal line.

three empty spheres for bcc. We recalculated the lifetimes for some representative examples (potassium, molybdenum, niobium, aluminum, and copper) and found that they are almost independent of the way in which space is divided; the lifetimes change by less than 3 ps in all cases, confirming that the ASA gives an adequate description of the positron wave function and potential.

The core and valence contributions to the annihilation rate for the two treatments of the enhancement factor are presented in Table II. In general, the core is taken to be the last-closed rare-gas-atom shell of electrons. The total annihilation rate is clearly dominated by annihilations with the valence electrons. The core annihilation generally contributes only 5–12 % of the total rate for Eq. (5) and 15–25 % for Eq. (1). This pronounced sensitivity to the valence-band electrons makes positron annihilation a valuable tool for studying the Fermi surfaces of metals.[18] Even when the valence electrons comprise only a small fraction of the total number of electrons in the system, they still account for more than 75% of all the annihilations. Positrons annihilate mostly with the valence electrons because of the strong Coulomb repulsion between the positron and the nucleus. This pushes the positron wave function out to the interstitial region where the overlap with the core electrons is minimal. This is illustrated in Fig. 2 where the radial part of the positron charge density is plotted together with core- and valence-electron charge densities for palladium.

For the transition metals, the core contribution tend to increase toward the middle of the transition-metal series and fall off at either end. This is due to the different rates of contraction of the core and the lattice constant. Toward the beginning of the series, both the core and the lattice constant contract with increasing atomic number, but the lattice constant decreases more rapidly so that the core actually occupies a larger fraction of the unit-cell

TABLE I. Positron lifetimes in ps for a variety of elemental metals and monovacancies.

Element	Eq. (5)	Eq. (1)	Experiment[a]
Alkali metals			
Lithium	311	295	291
Sodium	348	319	338
Potassium	394	363	397
Rubidium	403	372	406
Cesium	414	385	418
3*d* transition metals			
Titanium	159	143	147
Vanadium	127	115	130
Chromium	109	101	120
Iron	107	101	106
Nickel	102	97	110
Copper	107	103	110
4*d* transition metals			
Zirconium	174	156	165
Niobium	135	121	119
Molybdenum	114	104	103
Palladium	109	103	96
Silver	125	120	131
5*d* transition metals			
Tantalum	129	116	116
Tungsten	110	100	105
Platinum	101	96	99
Gold	112	108	117
Other metals			
Aluminum	170	163	163
Lead	189	187	194
Gadolinium	221	199	230
Vacancies[b]			
Al vacancy	239	234	244
Cu vacancy	169	164	173
Ag vacancy	199	194	198

[a] Reference 13.

[b] Vacancy experimental values from Refs. 14–16.

TABLE II. Annihilation rates (in ns^{-1}).

Element	Eq. (5) Core	Eq. (5) Valence	Eq. (1) Core	Eq. (1) Valence
Alkali metals				
Lithium	0.166	3.053	0.483	2.911
Sodium	0.245	2.628	0.762	2.373
Potassium	0.161	2.379	0.768	1.984
Rubidium	0.149	2.330	0.818	1.863
Cesium	0.130	2.286	0.857	1.738
3*d* transition metals				
Titanium	0.698	5.604	1.784	5.201
Vanadium	0.907	6.963	2.137	6.526
Chromium	1.011	8.122	2.255	7.686
Iron	0.825	8.491	1.722	8.172
Nickel	0.756	9.095	1.479	8.836
Copper	0.628	8.701	1.201	8.494
4*d* transition metals				
Zirconium	0.613	5.150	1.710	4.718
Niobium	0.840	6.577	2.129	6.101
Molybdenum	0.963	7.777	2.315	7.288
Palladium	0.663	8.545	1.401	8.272
Silver	0.481	7.498	1.010	7.298
5*d* transition metals				
Tantalum	0.962	6.804	1.877	6.327
Tungsten	1.027	8.085	2.356	7.629
Platinum	0.693	9.249	1.436	8.984
Gold	0.523	8.380	1.076	8.178
Other metals				
Aluminum	0.267	5.622	0.603	5.520
Lead	0.101	5.187	0.201	5.149
Gadolinium	0.440	4.087	1.372	3.661
Vacancies				
Al vacancy	0.097	4.086	0.223	4.046
Cu vacancy	0.270	5.659	0.526	5.565
Ag vacancy	0.194	4.819	0.415	4.734

volume. The positron wave function, which is mostly in the interstitial region, therefore increases its overlap with the core, and the annihilation rate is raised. Maximum overlap is achieved close to the middle of the transition-metal series. As we continue to increase the atomic number, the lattice constant decreases more slowly, and even begins to expand again towards the end of the series, while the core continues to contract. The core-annihilation rate is accordingly reduced as the positron overlap with the core decreases, giving rise to the observed behavior.

A comparison of the two approximations for the core-enhancement factor indicates that while there are significant differences in the core contribution to the annihilation rate, the resulting lifetimes are roughly comparable and in almost equally good agreement with experiment, although the all-enhanced results from Eq. (1) always give lower lifetimes than the IPM-core plus enhanced-valence calculations of Eq. (5). The increased core-annihilation rate in the all-enhanced case is slightly

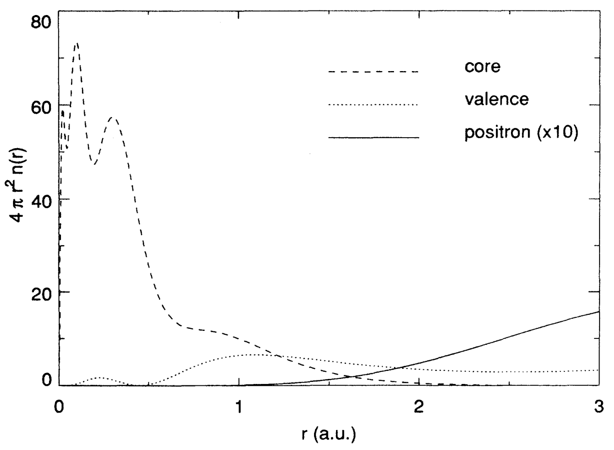

FIG. 2. Radial part of the core- and valence-electron densities and positron density for fcc palladium.

offset by a reduction in the valence-band annihilation due to the inclusion of the core charge density in the calculation of the enhancement factor $\Gamma[n(\mathbf{r})]$, since, from Eq. (4), the enhancement factor decreases with increasing charge density. It is difficult to decide which of these procedures provides the better description in general. Equation (1) is formally more elegant, but it certainly overestimates the response of the core to the positron, since these tightly bound electrons are not nearly as polarizable as the free-electron gas, which is used to calculate the enhancement. In addition, the valence-band response is probably underestimated due to the reduction in the enhancement factor mentioned above. In contrast, the IPM-core plus enhanced-valence calculation of Eq. (5) is probably more accurate for the valence electrons but is surely an underestimate of the core contribution. Theoretical calculations suggest that a core-enhancement factor in the range of 1 to 2 is appropriate,[12] so a reasonable argument can be made for adopting an average enhancement on the core of 1.5, as suggested by Puska and Nieminen.[3] The average-core-enhancement values obtained in the all-enhanced calculation are somewhat larger,[19] in the range of 2–3, and these appear to be in reasonable accord with theoretical estimates based on a polarizability model for the core.[20] Experimental estimates of the core enhancement based on the high-momentum components of the two-dimensional angular correlation of annihilation radiation spectrum have been made,[18] but these are difficult to interpret with any certainty, and those that have been made tend to favor lower values for the enhancement factor.[21] In general, we find that the IPM-core plus enhanced-valence procedure of Eq. (5) gives slightly better agreement with experiment, so in the absence of a more realistic theory, we prefer to use this approximation. This is not inconsistent with the use of the density functional theory (DFT), where functionals depend on the total electron density rather than on valence and core charge decompositions, since the enhancement factor, which is related to the polarizability, is not rigorously determined in this form by DFT. This approximation assumes that the polarization of the slowly varying charge density in the region sampled by the positron is well described by the polarization of a constant charge density and would have no validity if the positron overlapped strongly with the rapidly varying charge density closer to the nucleus.

Although we prefer to use the results of Eq. (5), the all-enhanced calculations are nevertheless informative. The two calculated lifetimes give useful upper and lower estimates for the true lifetime. In addition, if we wanted to consider the relative probability of annihilation with two different core states, the results of Eq. (1) may provide a more realistic description of the orbital-dependent enhancement than the IPM calculations due to the charge density dependence of the enhancement factor.

The difference in the two procedures depends to some extent on the choice of the core. In the trivial extreme case where we choose all the electrons to be treated as valence, there will be no difference in the two calculations. The more electrons are treated as valence, the smaller the differences between the two approximations. We see this clearly in calculations on titanium and lead. In the case of titanium, it seems reasonable to treat the $3p$ electrons as core electrons. If we do this, there is a difference of 16 ps between the results of Eqs. (1) and (5). If, on the other hand, we decide that the $3p$ electrons should be treated as valence electrons, there is a difference of only 2 ps between them. This suggests that the enhancement factor of the $3p$ core should be somewhat larger than the IPM value in this case. A similar problem arises for lead. In Table II the reported value is calculated assuming that the $5d$ electrons belong to the valence charge density. The difference in the calculated lifetime is only 2 ps. This increases to 22 ps when we recalculate with the $5d$ electrons treated as part of the core. The choice of the core generally creates the single biggest source of uncertainty in these calculations. The resolution of this problem must ultimately lie in a more sophisticated treatment of the many-particle interactions involved in the calculation of the enhancement factor.

The description of these many-body interactions is also expected to affect the lifetimes seen in semiconductors and insulators. For nonmetallic systems, the positron wave function can still be calculated using the procedure outlined above, with the same validity as the application of LDA to electron calculations in these systems, which are known to be highly successful.[22] The enhancement factor, however, must be calculated by taking into account the different nature of the polarizability in an insulator as opposed to a metal. In electronic-structure calculations on semiconductors, the LDA imposes a metalliclike screening which is responsible for the well-known underestimate in the calculated energy gap. A more accurate treatment of the screening restores the correct gap.[23–25] In a similar way, the local density form of the enhancement factor in Eq. (4) presupposes a metallic screening, and this must be modified to give an appropriate description of the enhancement factor in nonmetallic systems. Some simple models based on atomic polarizabilities have been proposed to account for this.[26]

In order to get an estimate of the lifetime of a positron trapped in a metal vacancy, we performed calculations on undistorted vacancies by taking a simple cubic cell containing four atoms arranged on an fcc lattice and removing one atom to form the monovacancy. This corresponds to putting vacancies a distance a apart at the corners of a cubic cell, with atoms in the face-center positions. Since this is a fairly small supercell with a large concentration of vacancies, we repeated the calculations with an eight-atom fcc cell, where the vacancies are a distance $a\sqrt{2}$ apart, and occupy four of the eight corners of the cube. The Al vacancy lifetimes reduced by about 3%, suggesting a small spread in the positron wave function around the vacancy site. The lifetimes for the Cu and Ag vacancies were totally unaltered, indicating that the positron is so strongly trapped by the vacancy that the results are not significantly affected by vacancy-vacancy iterations introduced by the supercell geometry. In general, accurate values of the lifetime may therefore be obtained from fairly modest-sized electronic-structure calculations.

The vacancy calculations were performed using the same electron-positron interactions as have been used in the bulk calculations. In principle, this is incorrect, since the equations for the electron-positron interactions have been derived under the assumption that the positron is delocalized and so does not alter the electron charge density prior to annihilation. Once the positron becomes localized in a defect, the electrons in that environment will be attracted by the increased positive charge, producing a significant change in both electron and positron charge densities. Furthermore, the expressions for the electron-positron interactions must be altered to take account of the finite-positron charge density in the localized defect. Nieminen, Boroński, and Lantto[27] have considered these effects and conclude that the increase in the annihilation rate due to the charge relaxation around the positron is roughly compensated by the reduction in the enhancement factor calculated for the two-component electron-positron gas. This justifies our use of this approach in the vacancy calculations.

IV. CONCLUSIONS

We have presented a first-principles method for calculating the bulk positron lifetimes in solids. The electron-positron interaction parameters have all been taken from first-principles many-body calculations and convenient expressions for the electron-positron correlation potential and enhancement factor have been presented. We find very good agreement with experiment for the systems we have considered, which encompass a wide range of elemental metals. We also find good agreement for vacancy calculations, and even for the intermetallic alloy Ni_3Al. This gives us the confidence to apply our method as a predictive tool in metallic systems where the bulk lifetime is not known in advance, or where there may be some suspicion that the annihilation is defect related instead of bulklike. Recent calculations[28] on the high-temperature superconductor $K_xBa_{1-x}BiO_3$ have demonstrated the versatility and reliability of this approach, as well as its value in interpreting experimental data.

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[1] R. W. Siegel, in *Positron Annihilation,* edited by P. G. Coleman, S. C. Sharma, and L. M. Diana (North-Holland, Amsterdam, 1982), p. 351; K. Petersen, in *Positron Solid-State Physics,* edited by W. Brandt and A. Dupasquier (North-Holland, Amsterdam, 1983), p. 298.

[2] W. Brandt and J. Reinheimer, Phys. Lett. **35A**, 109 (1971).

[3] M. J. Puska and R. M. Nieminen, J. Phys. F **14**, 1299 (1984).

[4] K. O. Jensen, J. Phys. Condens. Matter **1**, 10595 (1989).

[5] B. Chakraborty, Phys. Rev. B **24**, 7423 (1981).

[6] E. Boroński and R. M. Nieminen, Phys. Rev. B **34**, 3820 (1986).

[7] B. Chakraborty and R. W. Siegel, Phys. Rev. B **27**, 4535 (1983).

[8] H. L. Skriver, *The LMTO Method,* Springer Series in Solid State Sciences Vol. 41 (Springer, New York, 1984).

[9] See, e.g., W. Kohn and P. Vashista, in *Theory of the Inhomogeneous Electron Gas,* edited by S. Lundqvist and N. H. March (Plenum, New York, 1983).

[10] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[11] J. Arponen and E. Pajanne, Ann. Phys. (N.Y.) **121**, 343 (1979).

[12] E. Bonderup, J. U. Anderson, and D. N. Lowy, Phys. Rev. B **20**, 883 (1979).

[13] A. Seeger, F. Barnhart, and W. Bauer, in *Positron Annihilation,* edited by L. Dorikens-Vanpraet, M. Dorikens, and D. Segers (World Scientific, Singapore, 1989), p. 275.

[14] M. J. Fluss, L. C. Smedskjaer, M. K. Chason, D. G. Legnini, and R. W. Siegel, Phys. Rev. B **17**, 3444 (1978).

[15] R. H. Howell, Phys. Rev. B **18**, 3015 (1978).

[16] R. H. Howell, Phys. Rev. B **24**, 1835 (1981).

[17] M. Shimotomai, T.-M. Wang, T. Iwata, and M. Doyama, in *Positron Annihilation,* edited by P. C. Jain, R. N. Singru, and K. P. Gopinathan (World Scientific, Singapore, 1985), p. 140.

[18] R. N. West, Adv. Phys. **22**, 263 (1973).

[19] This average-core-annihilation rate can be calculated directly from Table II by dividing the core-annihilation rate for Eq. (1) by IPM core value from Eq. (5).

[20] M. Šob, Solid State Commun. **53**, 235 (1985).

[21] K. G. Lynn, J. R. MacDonald, R. A. Boie, L. C. Feldman, J. D. Gabbe, M. F. Robbins, E. Bonderup, and J. Golovchenko, Phys. Rev. Lett. **38**, 241 (1977).

[22] U. von Barth and A. R. Williams, in *Theory of the Inhomogeneous Electron Gas* (Ref. 8).

[23] P. A. Sterne and J. C. Inkson, J. Phys. C **17**, 1497 (1984).

[24] W. E. Pickett and C. S. Wang, Phys. Rev. B **30**, 4719 (1984).

[25] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **34**, 5390 (1986).

[26] M. J. Puska, S. Mäkinen, M. Manninen, and R. M. Nieminen, Phys. Rev. B **39**, 7666 (1989).

[27] R. M. Nieminen, E. Boroński, and L. J. Lantto, Phys. Rev. B **32**, 1377 (1985).

[28] P. A. Sterne, J. C. O'Brien, R. H. Howell, and J. H. Kaiser, in *Defects in Materials,* edited by P. D. Bristowe, J. E. Epperson, J. E. Griffith, and Z. Lilental-Weber, MRS Symposia Proceedings No. 209 (Materials Research Society, Pittsburgh, 1991).