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New approach to the positron distribution in metals and alloys*

M. J. Stott and P. Kubica
Physics Department, Queen's University, Kingston, Ontario, Canada

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A positron pseudopotential is proposed that simplifies the description of a thermalized positron in a metal or alloy. The method is based on a factorization of the positron wave function into an energy-independent core function, which accounts for the detailed behavior of the positron when it approaches an ion core, and a smooth envelope or pseudo wave function. The pseudo wave function satisfies a Schrödinger-like equation with a relatively weak potential—the pseudopotential. Pseudopotential differences have been calculated for a number of alloys. The results indicate that the positron may have a strong preference or affinity for one sort of atom in binary alloys over the other. This relative positron affinity should lead to the positron preferentially annihilating with the electrons of that sort of atom in the alloy, and a method of detecting this from measured positron-annihilation data is proposed.

I. INTRODUCTION

Positron-annihilation techniques have resulted in much useful information on the electron behavior in pure metals.[1] The positron initially with a large energy ~1 MeV rapidly looses energy in the sample, and the bulk of the annihilation processes take place when the positron is roughly in thermal equilibrium with the sample. The positron lifetime can be measured yielding information on the electron density at the position of the positron, and in addition, the angular correlation of the two γ rays resulting from the most probable decay process can be measured. This yields information on the momentum distribution of the annihilating positron-electron pair. The spatial distribution of the annihilating positron in pure metals plays a minor role in the interpretations of most experiments; the slight penetration of the positron into the ion-core regions merely leads to a small core-electron contribution to the positron annihilation in simple metals.[2] In some systems the spatial distribution of the positron is an important factor in the interpretation of positron-annihilation experiments. In these cases the localization of the positron in atypical regions of the sample and its subsequent annihilation there dominates the measured positron-annihilation characteristics. For example, at a temperature of about 600 °C the equilibrium concentration of monovacancies in Al, $\sim 10^{-4}$, is sufficiently high that more than 95% of thermalized positrons annihilate from bound states in the immediate vicinity of vacancies because of the strong positron-vacancy interaction.[3] Positron trapping at vacancies in Cu, Ag, Au, Mg, Zn, Cd, Al, In, Tl, and Pb has so far been detected.[4] Effects due to positron trapping at dislocations[5,6] and at voids[7] in some metals have also been reported.

Positron-annihilation experiments have also been performed on alloys with the aim of studying changes with composition of the electron momentum distribution, in particular, the Fermi surface. Results of Stewart[8] on disordered LiMg alloys indicated an increase in the Fermi momentum on increasing the Mg concentration. More recently, many Fermi-surface studies have been carried out on alloys such as CuZn.[1] Positron annihilation is a valuable tool for studing these systems since the short electron mean free path prohibits the use of the precise techniques (such as de Haas–van Alphen) used for pure metals or very dilute alloys. However, little is known about the spatial distribution of thermalized positrons in alloy systems.

In this paper a theoretical framework is presented for calculating the distribution of the thermalized positron in pure metals, pure metals with point defects, and in substitutional alloys. In the following paper the method is used in a detailed discussion of the results of positron-annihilation experiments performed on a series of LiMg alloys. The method can also be used for calculating accurate positron wave functions and energies for perfect metals including full lattice symmetry.

Since the early calculations of positron ground-state wave functions in metals using the Wigner-Seitz approximation[2] it has been evident that the spatial distribution of the thermalized positron has something of a "Swiss cheese" character, the distribution being relatively uniform apart from "holes" around each ion due to the strong repulsion of the positron from the positively charged ions. This qualitative picture will be put on a quantitative footing in the following sections by describing the positron distribution in terms of a smooth envelope modulated by a function which is small in the region of each ion core.

The positron wave function for states near the bottom of the lowest positron energy band is separated into two factors. One factor reflects the strong repulsion of the positron from the ion core. It is insensitive to the energy of the positron and to the environment of the ion core. The other factor is a smooth envelope function which is energy dependent and sensitive to the environment. The envelope satisfies a Schrödinger-like equation with a relatively weak potential term. The philosophy adopted prompts the use of the term pseudopotential for this weak potential and positron pseudo wave function for the smooth envelope.

The positron pseudopotential for a substitutional alloy will be different in atomic cells containing different sorts of atoms. This will lead to an enhancement of the pseudo wave function at the more attractive site and an over-all preference of the positron for one atom or the other in a binary alloy. The positron pseudopotential difference between different sorts of cells is proposed as a measure of the relative positron affinity. This affinity should lead to the positron preferentially annihilating with the electrons of one sort of atom over the other, and a method of detecting this preference from observed quantities has been devised.

The method is based on a comparison of the contribution that electrons in the ion-core regions make to the positron annihilation in the alloy and in the two pure metals. The contribution that these electrons make to the total positron-annihilation rate is termed the positron-core-annihilation rate and this quantity for the alloy can, to a good approximation, be written in terms of the core rates for the two pure metals and the positron pseudodensity distribution in the alloy.

In Sec. II the pseudopotential picture of a positron is presented. The case of a positron in a pure metal is discussed and then the case of a positron in a substitutional binary alloy is presented. In Sec. III calculations of positron pseudopotential differences between the two components of a number of alloys are presented and the relative affinity of the positron for one sort of atom or the other is discussed. The core rate is discussed in Sec. IV, and core rate in an alloy is expressed in terms of the positron pseudo wave function. Conclusions are drawn in Sec. V.

II. POSITRON PSEUDOPOTENTIAL PICTURE

The basic ideas and the method will be introduced by considering the case of a thermalized positron in a perfect metal. The generalization to the case of a metal with point defects or a substitutional alloy will then be straightforward. Attention will be focused on simple metals for which a clear distinction can be made between core and valence electrons, but some qualitative conclusions can be drawn for the noble metals.

It is somewhat easier to construct an approximate single-particle potential in which a thermalized positron moves in a metal than it is for an electron in a metal. There is, of course, no Pauli repulsion between the positron and an electron and so there is no exchange contribution to the positron potential. Furthermore, calculations[9] based on a positron in a uniform electron gas indicate that the positron-electron correlation energy is a slowly varying function of mean electron density in the range of metallic densities. This means that the positron correlation potential in the interstitial regions of the metal will be relatively constant. In the high-electron-density regions in the ion cores, the correlation potential will be swamped by the larger Hartree potential. To a good approximation the positron in a metal moves in the Hartree field of the ions and conduction electrons. The Hartree potential $V(\vec{r})$ for the positron in a metal can be estimated using the charge density of the ions and a knowledge of the valence-electron density. The former can be constructed from calculated free-atom wave functions which are sufficiently accurate for our purposes. The valence electrons in simple metals are believed to be fairly uniformly distributed, and to a reasonable approximation their contribution may be calculated assuming a uniform distribution.

The single-particle wave function $\psi(\vec{r})$ for a low-lying positron state of energy E satisfies the Schrödinger equation

$$(-\hbar^2/2m)\nabla^2\psi(\vec{r}) + [V(\vec{r}) - E]\psi(\vec{r}) = 0 \ . \tag{1}$$

The positron, having a positive charge, is strongly repelled from the ion-core regions of a metal and consequently the wave function is small in these regions, increasing rapidly to become largest in the regions between the ions. Calculations of positron wave functions for the state at the bottom of the lowest energy band for a few metals have been made using the Wigner-Seitz approximation. The results indicate that the ratio of the positron density at the nucleus to that in the interstitial region is about 2% for Li and much smaller for the other metals, for example, 0.01% for Mg. It is clear that the positron wave function is not smooth and for many purposes a few plane waves would be a poor representation in the core region. Similarly the potential experienced by the positron in these regions is large; its effect cannot be treated using low-order perturbation theory. In view of this it might seem puzzling that the bottom of the band effective mass ratio, m^*/m, for the positron is very near unity (m^*/m is 1.03 for Be and 1.05 for Na,[10] both calculations based on the Bardeen, Silverman, and Kohn method), implying that the positron, at least near to the bottom of the band, behaves rather like a free particle.

The free-particle nature of valence electrons in simple metals is reconciled with the very large attractive potential in the core region through the electron pseudopotential picture. The idea is that much of the large potential the valence electron experiences in the core region is cancelled by the kinetic energy arising from the necessary orthogonality to the core-electron states. The residual part of the potential is known as the electron pseudopotential, and the corresponding pseudo wave function is relatively smooth. An analogous situation does not exist for the thermalized positron since we are only concerned with the lowest single-particle positron states.

In the core regions where the positron wave function is most distorted the potential $V(\vec{r})$ is much larger than the positron energies of interest (a few eV only) and so from (1) the shape of $\psi(\vec{r})$ in the core regions must be insensitive to the positron energy. Therefore, a positron core function, with the correct spatial dependence in the core regions, and independent of positron energy is factorized out of the positron wave function $\psi(\vec{r})$ to leave a smooth envelope. This envelope contains all the energy dependence of $\psi(\vec{r})$, and we adopt for it the term positron pseudo wave function.

For a positron in a perfect metal we write

$$\psi(\vec{r}) = U_0(\vec{r}-\vec{R})\,\psi^{\text{pseudo}}(\vec{r}) \ , \qquad (2)$$

where $\vec{r}$ lies within an atomic cell centered on $\vec{R}$ and $U_0(\vec{r})$ is the positron Wigner-Seitz wave function. Ideally, the exact positron bottom of the band wave function would be chosen for the positron core function, but since these are relatively difficult to calculate, we would defeat our object of devising a simple scheme to compute positron distributions. The positron Wigner-Seitz wave function is the lowest S-like radial wave function that is flat at the surface of the equal volume sphere, and so it does not exactly satisfy the Schrödinger equation near the cell boundaries. However, detailed calculations[11] performed for Al indicate that the positron Wigner-Seitz energy E_0 differs by only 0.01 Ry from the exact bottom of the band energy and so we assume that

$$[(-\hbar^2/2m)\nabla^2 U_0(\vec{r}) + V(\vec{r})U_0(\vec{r})]/U_0(\vec{r}) = E_0 \qquad (3)$$

throughout the whole cell. Substituting (2) in the Schrödinger equation, we find that ψ^{pseudo} satisfies a Schrödinger-like equation

$$(-\hbar^2/2m)\nabla^2\psi^{\text{pseudo}}(\vec{r}) + \sum_n V^{\text{pseudo}}(\vec{r}-\vec{R}_n)\psi^{\text{pseudo}}(\vec{r}) = E\psi^{\text{pseudo}}(\vec{r}) \ , \qquad (4)$$

where V^{pseudo} the quantity playing the role of the potential, which will be termed the positron pseudopotential, consists of two parts and is given by

$$\begin{aligned} V^{\text{pseudo}}(\vec{r}) &= E_0 - \frac{\hbar^2}{m}\left(\frac{d}{dr}\ln U_0(r)\right)\hat{r}\cdot\nabla \ , \\ &\qquad \text{for } \vec{r} \text{ within the atomic cell} \\ &= 0, \qquad \text{for } \vec{r} \text{ outside the atomic cell.} \qquad (5) \end{aligned}$$

The first part is constant throughout the cell and for the perfect metal has the same value in every cell. With the zero of energy taken to be the value of the electrostatic potential in the interstitial region (at $r = R_a$) the Wigner-Seitz energies are large and positive. Values of E_0 for a number of metals are listed in Hodges and Stott.[9] The second part, which we shall term the gradient part of the pseudopotential and denote by $V_G(\vec{r})$, is more complicated. However, it is easy to see that it is much weaker than $V(\vec{r})$ in the core region. Whereas the full potential diverges near the nucleus having the form $V(\vec{r}) \sim Z/r$, the logarithmic derivative $U_0^{-1}(r)dU_0(r)/dr$ entering V_G remains finite and has the value $Ze^2m/\hbar^2$ at $r = 0$ and falls sharply to zero at the equal volume cell radius since $U_0(r)$ is flat there. But the major point is that the contribution of V_G to the positron energy depends on the gradient of ψ^{pseudo} which is small because the rapidly varying part of the full wave function in the core region has been factorized out. The error introduced into V_G due to the use of the approximate Wigner-Seitz wave function in (2) and (3) is small because in the region near the cell boundary where $U_0(\vec{r})$ does not have the full lattice symmetry and is poorest, V_G is small. The positron Wigner-Seitz wave functions and logarithmic derivatives for Li and Mg are illustrated in Fig. 1; the normalization of the wave functions has been adjusted so that $U_0(R_a) = 1$.

The Wigner-Seitz method for obtaining the bottom of the band wave function is a better approximation for the $\vec{k} = 0$ valence electron state in a cubic metal than it is for the positron. The greater curvature in the positron wave function near the cell boundary arises from the exclusion of the positron from the central part of the cell and results in the large values for E_0. The electron Wigner-Seitz wave function in the case of an alkali metal is flat over 90% or more of the cell volume.[12] The logarithmic derivative of the valence-electron Wigner-Seitz wave function will be small over most of the cell, and it might seem tempting to

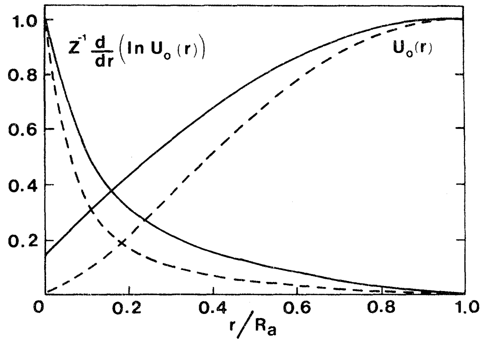

FIG. 1. Positron Wigner-Seitz wave functions and their logarithmic derivatives for Li (full lines) and Mg (dashed lines) plotted against r/R_a. The wave functions are normalized so that $U_0(R_a)=1$.

construct a pseudopotential and pseudo wave function for the electron following a procedure similar to (2), (4), and (5). The drawback to this is that the nodes in the core region of the valence-electron wave function lead to divergences in its logarithmic derivative and hence also in the $V_G(\vec{r})$. Consequently the form factor corresponding to $V_G(\vec{r})$ will oscillate and decrease slowly for large momentum transfers. The factorization of the valence-electron wave function into an energy-independent core part and a smooth envelope is not useful because the nodes in the electron wave function in the ion-core region shift with energy. In contrast to the electron case, the positron states of interest lie near the bottom of the lowest band and the positron Wigner-Seitz function has no nodes; $V_G(\vec{r})$ is well-behaved.

The validity and usefulness of a pseudopotential picture for positrons in metals, and as we shall see later in alloys also, hinges on the awkward part of the positron pseudopotential $V_G(\vec{r})$ being small enough to be treated in low-order perturbation theory. The positron band effective mass at $k=0$ has been calculated for a number of simple metals in order to test this.

In the case of pure metals, the constant part of the positron pseudopotential (since it has the same value in every atomic cell) leads merely to a uniform potential of magnitude E_0 throughout the metal. The positron $E(\vec{k})$ relation would then be free-particle-like with $E(\vec{k})=E_0+\hbar^2k^2/2m$; the corresponding positron pseudo wave function would be a plane wave $e^{i\vec{k}\cdot\vec{r}}$. Any deviation of the positron $E(\vec{k})$ relation from free-particle-like behavior, in particular the deviation of the effective mass relation m^*/m from 1, must be due to the gradient part of the pseudopotential V_G. Conventional perturbation theory to second order in V_G leads to an expression for the positron $E(\vec{k})$ relation,

$$E(\vec{k})=E_0+\frac{\hbar^2k^2}{2m}+\frac{1}{\Omega^2}\sum_{n\neq0}\frac{|S(\vec{K}_n)|^2|\langle\vec{k}+\vec{K}_n|V_G|\vec{k}\rangle|^2}{\hbar^2k^2/2m-(\hbar^2/2m)(\vec{k}+\vec{K}_n)^2}, \tag{6}$$

where Ω is the volume of the unit cell, $\vec{K}_n$ is a reciprocal lattice vector, $S(\vec{K}_n)$ is the structure factor, and

$$\langle\vec{p}|V_G|\vec{q}\rangle=-\int d\vec{r}\,e^{-i\vec{p}\cdot\vec{r}}\;V_G(\vec{r})e^{i\vec{q}\cdot\vec{r}}\;. \tag{7}$$

The matrix element can be simplified to give

$$\langle\vec{p}|V_G|\vec{q}\rangle=\frac{4\pi\hbar^2}{m}\frac{\vec{q}\cdot(\vec{p}-\vec{q})}{|\vec{p}-\vec{q}|}\times\int_0^{R_a}dr\,r^2\frac{d}{dr}[\ln U_0(r)]\,j_1(|\vec{p}-\vec{q}|r), \tag{8}$$

where

$$j_1(x)=(\sin x)/x^2-(\cos x)/x$$

is the second spherical Bessel function. Near the bottom of the positron band, that is for small $\vec{k}$, (6) simplifies and we have

$$E(\vec{k})=E_0+\frac{\hbar^2k^2}{2m}-\frac{\hbar^2}{2m}\sum_{n\neq0}|S(\vec{K}_n)|^2\times A^2(K_n)\left(\frac{\vec{k}\cdot\vec{K}_n}{K_n^2}\right)^2\frac{4}{K_n^2}\;, \tag{9}$$

where

$$A(K_n)=\frac{4\pi K_n}{\Omega}\int_0^{R_a}dr\,r^2\frac{d}{dr}[\ln U_0(r)]j_1(K_nr). \tag{10}$$

The final expression for the positron effective mass ratio at $k=0$ for the cubic metals is

$$\frac{m^*}{m}=1+\frac{4}{3}\sum_{n\neq0}|S(\vec{K}_n)|^2\left(\frac{A(K_n)}{K_n^2}\right)^2\;. \tag{11}$$

The quantity $A(q)$ plays the role of the positron

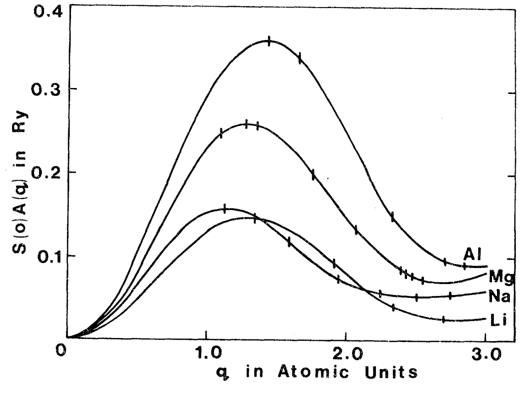

FIG. 2. Positron pseudopotential coefficients $S(0)\,A(q)$ in rydbergs [Eq. (10)] plotted against q in atomic units for Li, Na, Mg, and Al.

TABLE I. Positron $\vec{k}=0$ effective masses calculated to second order in the positron pseudopotential using Eq. (11). Values calculated previously for Be and Na by Stewart *et al.* (Ref. 10) are in parentheses.

	Li	Na	K	Be	Mg	Al
m^*/m	1.03	1.07(1.05)	1.11	1.04(1.03)	1.10	1.12

pseudopotential form factor, and it is illustrated for a number of cases in Fig. 2. The positron effective mass ratios calculated using (11) for a number of metals are given in Table I. The positron effective mass ratios for Be and Mg were estimated by spherically averaging the $E(\vec{k})$ relation. In this way average scalar instead of tensor effective masses were obtained. They increase as the size of the core increases and also are larger for polyvalent metals although in all cases considered they deviate little from unity. In those cases where m^*/m has previously been calculated using the Bardeen-Silverman-Kohn small-$\vec{k}$ expansion, namely Be and Na, there is good agreement. This agreement indicates that second-order perturbation theory in V_G is working well, and furthermore the small deviation of m^*/m from unity confirms that V_G is small.

A more exhaustive test of the positron pseudopotential picture has been carried out.[11] Using a slightly modified pseudopotential the $\vec{k}=0$ positron wave function including the full lattice symmetry has been calculated up to first order in the gradient part of the pseudopotential. These wave functions have been compared with the results of diagonalizing the secular equation with a plane wave basis and using the matrix elements of the full potential. The perturbative results are as good as these and near the nucleus are superior. The $\vec{k}=0$ energies have also been calculated using both methods, and the results are in excellent agreement. The details of these calculations will be presented elsewhere.[11]

The calculation of positron wave functions in alloys is a harder problem, and this will be discussed now in the light of the positron pseudopotential picture. Consider a thermalized positron in an A-B substitutional alloy. The positron potential consists of four contributions:

(a) The bare-ion contributions described earlier.

(b) The Hartree contribution from the valence electrons which for a particular atom we have smeared out uniformly over its atomic cell so that at this stage each cell is electrically neutral.

(c) The contribution from positron–valence-electron correlations. Even in an alloy of simple metals there will be considerable nonuniformity of the valence-electron density if there is a valence difference, and since the positron-electron correlation energy varies, albeit slowly, with electron density, there will be a contribution to the positron potential. A local density approximation has been used to estimate this contribution and a term $E_{\text{corr}}(\rho(\vec{r}))$ has been added to the potential, where $E_{\text{corr}}(\rho(\vec{r}))$ is the positron-electron correlation energy for a uniform electron gas of density ρ, and $\rho(\vec{r})$ is the valence-electron density in the alloy which is assumed to be uniform within each cell, but will have a different value in cells of different valency. This will amount to a term E^x_{corr} in the potential within a cell, where the type of cell has been denoted by $x=A$ or B.

(d) The contribution due to charge transfer from one type of cell to another. An accurate estimate of this contribution would require the valence-electron density in the alloy. A calculation of this quantity would be very difficult and little information is as yet available; so the potential due to charge transfer has been estimated using the following simple argument.

Consider a large isolated cluster of A atoms in B metal. Electron relaxation results in charge transfer across the cluster boundary and a charge dipole layer is set up around the cluster. There is no simple way of determining the amount of charge transferred; however, the additional Hartree potential due to the dipole layer is just sufficient to equalize the internal Fermi energies inside and outside the cluster. In this case the potential due to charge transfer experienced by the positron apart from an unimportant constant is approximately given by E^A_F inside the A cluster and E^B_F outside, where E^A_F and E^B_F are the internal electron Fermi energies of the A and B metals, respectively. This prescription is used for calculating the Hartree potential due to charge transfer around a single cell, although we realize that the extent of the dipole layer is only slightly smaller than the dimensions of the atomic cell. Splitting up the alloy into atomic cells each of the same volume, the potential due to charge transfer is approximated by a constant potential E^A_F in every cell occupied by an A atom and E^B_F in the B atom cells. Here E^A_F and E^B_F are the internal Fermi energies for the A and B metals each adjusted to the alloy atomic volume. Similar arguments to these have been used to discuss electrochemical effects in alloys[13] and to estimate the potential experienced by electrons due to charge transfer in dilute alloys.[14]

The positron potential in, say, an A cell of the alloy is, apart from a constant, the same as that in a cell of the pure A metal adjusted to have the alloy atomic volume. This means that the wave function for a thermalized positron near an A ion in the alloy is very similar in shape, though we shall see not in amplitude, to the wave function near an A ion in the pure A metal, and similarly for the B ions. The pseudopotential picture for a thermalized positron, applied earlier to a pure metal can be applied to the alloy. The Wigner-Seitz wave function for a positron in an A cell, U_0^A, is factorized out of the full positron wave function ψ in each A cell and similarly for the B type cells,

$$\psi(\vec{r}) = U(\vec{r})\psi^{\text{pseudo}}(\vec{r}) \quad , \tag{12}$$

where

$$U(\vec{r}) = U_0^x(\vec{r} - \vec{R}) \tag{13}$$

for $\vec{r}$ within the cell of type x, either A or B, centered on the site $\vec{R}$. The amplitude of the Wigner-Seitz solutions is adjusted so that the solutions for the different sorts of cell have the same value in the interstitial region $U_0^A(R_a) = U_0^B(R_a)$. This means that the Wigner-Seitz solutions for different cells no longer have the same normalization, and we write

$$\alpha^x = \int_\Omega d\vec{r}\,[U_0^x(r)]^2 \ , \tag{14}$$

where $\int_\Omega d\vec{r}$ denotes the integration over the atomic cell (the Wigner-Seitz sphere in the approximate scheme). Taking $\psi^{\text{pseudo}}(\vec{r})$ equal to a constant in (12) would give the simplest approximation for the positron wave function in the alloy. Improvements to this can be calculated from the Schrödinger-like equation satisfied by ψ^{pseudo}. Following a similar procedure to that outlined for the pure metal ψ^{pseudo} is given by (4) where the positron pseudopotential for the alloy is

$$V^x(\vec{r}) = E_0^x + E_F^x + E_{\text{corr}}^x - \frac{\hbar^2}{m}\left(\frac{d}{dr}\ln U_0^x(r)\right)\hat{r}\cdot\nabla \tag{15}$$

within a cell of type x, either A or B. The constant part of the positron pseudopotential has a different value in the different sorts of cell, the small gradient parts are also different and so the positron pseudo wave function will not be uniform throughout the alloy. The positron pseudo wave function and pseudopotential are indicated schematically in Fig. 3 and are compared with the full wave function and potential for the two cases of a positron in a pure metal and a positron in an alloy.

The positron pseudopotential may also be used to discuss the behavior of positrons near vacancies in metals. This case is also illustrated schematically in Fig. 3. Since there is no repulsive core in the vacancy cell, the factorization of the positron wave function is carried out in cells other than the vacant one, and the resulting positron pseudopotential is strongly attractive. The over-all picture is very similar to that proposed by Hodges,[15] although the positron trapping potential was deduced using different arguments. The positron-vacancy potential well depths calculated using these two approaches compare favorably.[16] In those metals where the positron-vacancy interaction is very strong leading to large positron-vacancy binding energies [for example in Al the positron-vacancy binding energy is about 2 eV (Ref. 15)] the positron bound-state pseudo wave function will be sharply localized and the gradient part of the pseudopotential which depends on $\nabla\psi^{\text{pseudo}}(\vec{r})$ may play a bigger role.

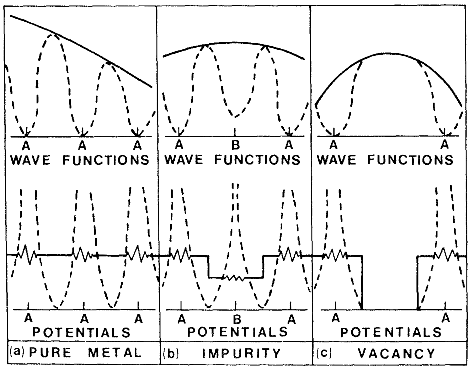

FIG. 3. A schematic figure illustrating the positron pseudo wave function and pseudopotential (full lines) and the corresponding full wave function and potential (broken lines) for three cases: (a) a positron in pure A metal, (b) a positron near an attractive substitutional impurity in A metal, and (c) a positron bound state at a monovacancy in metal. The jagged line is intended to represent the gradient part of the pseudopotential.

III. RELATIVE POSITRON AFFINITIES IN ALLOYS

Positron pseudopotential differences $V_0 = E_0^A - E_0^B + E_F^A - E_F^B + E_{\text{corr}}^A - E_{\text{corr}}^B$ have been calculated for a number of alloys with 50 at.% composition. The difference in the gradient part of the pseudopotentials have been neglected in view of the small deviation of m^*/m from unity for the pure metals and so the pseudopotential difference consists of the differences in the constant part, the charge transfer contribution, and the positron-electron correlation energy contribution.

The constant part of the pseudopotential E_0, merely the positron Wigner-Seitz energy for the alloy atomic volume, has been calculated by numerical integration of the radial Schrödinger equation. The potentials used were constructed from tabulated free atom electron wave functions[17] for the ion-core contribution and the potential due to the valence electrons uniformly distributed over the equal volume sphere. The correlation energy contribution has been estimated using results for the positron-electron correlation energy for a uniform electron gas calculated earlier by Hodges and Stott.[9] The internal Fermi energies used for calculating the charge transfer contribution were taken from Hodges and Stott.[13]

The positron pseudopotential difference has also been estimated for a AuAg alloy. The positron Hartree potential for this case requires further explanation. The outermost d-electron distribution was renormalized in the manner of Watson and Ehrenreich[18] so that ten d electrons were within the Wigner-Seitz sphere. As the positron penetrates into the d-electron shell, it experiences a rapidly increasing effective valence; so the positron wave function is rapidly varying in the outer regions of the cell. This means that the gradient part of the pseudopotential is much larger for the noble metals than it is for the simple metals with small ion cores. Consequently the band effective-mass ratio will also be larger for these metals. Perturbation calculations using (11) indicate effective-mass ratios of 1.11, 1.19, and 1.21 for Cu, Ag, and Au, respectively. The effective masses will probably be as large for the transition and rare earth metals. Even though the gradient parts of the pseudopotential are larger for Ag and Au, we do not believe that their omission in calculating the pseudopotential differences has lead to much error since the V_G for Ag and Au are rather similar. The internal electron Fermi energies for these metals were taken from Hodges and Stott.[9] The results for the positron pseudopotential difference are presented in Table II, a negative V_0 indicating a relative positron affinity for the A atom in the alloy.

The three contributions to V_0 are listed in columns 3–5 of Table II. The positron zero-point energy difference in column 3 arises from the interaction of the positron with the neutral cells. The positron tends to be pushed out of the cell containing the larger valence and larger ion core, for instance, out of the Mg cell in Li-Mg and out of the In cell in In-Cd. The effect of different ion cores is easiest to see in the alloys with no valence difference; for example, the positron is pushed away from the larger Zn ion in Mg-Zn alloy. There is some cancellation between the ion core and valence effects in Al-Zn; Al has the larger valence, but a smaller ion core and hence the relatively small zero-point energy difference. The next column lists the difference in positron-valence-electron correlation energy and here the effect is for the positron to be attracted to the cell with larger electron density, that is, to the cell with the larger valence. This tends to balance somewhat the valence contribution to the zero-point energy difference. Column 5 lists the contribution arising from electron charge transfer from one cell to another so that the cells are no longer electrically neutral. The magnitude and direction of the electron transfer is affected both by the electron kinetic energy, reduced if the electron wave functions are made more uniform, and the electron potential energy, which tends to pile up the electron wave functions in the cell with the more attractive electron pseudopotential.

The net result of these three contributions is to give substantial positron pseudopotential differences V_0 for most of the alloys considered. This means that the positron pseudo wave function will be enhanced in cells containing the component in italics in the following series of 50-at.% alloys of Al-*Zn*, Mg-*Al*, Mg-*Zn*, *Li*-Mg, Mg-*Cd*, In-*Cd*, and *Ag*-Au and positron-annihilation experiments should preferentially sample these components in the alloys.

The effect of the pseudopotential difference may easily be gauged. An isolated spherical potential well of depth V_0 and radius R_a will have at least one bound state (an s state) when

$$\lambda = R_a (2mV_0/\hbar^2)^{1/2}$$

is greater than $\pi/2$. The strength parameter λ has been calculated for the alloys considered, and they are listed in column 7 of Table II. A value of λ approaching 1 implies a substantial enhance-

TABLE II. Mean atomic radius, three contributions to the positron pseudopotential difference, and the net pseudopotential difference V_0 for a number of 50-at.% alloys. A negative V_0 in column 6 indicates a positron affinity for A over B in the alloy. The square-well strength parameter is also listed.

A B	R_a(a.u.)	$E_0^A - E_0^B$ (Ry)	$E_{\text{corr}}^A - E_{\text{corr}}^B$ (Ry)	$E_f^A - E_f^B$ (Ry)	V_0 (Ry)	λ
Al Zn	2.94	0.04	−0.04	0.08	0.08	0.8
Mg Al	3.09	−0.08	0.03	0.08	0.03	0.5
Mg Zn	3.06	−0.03	0.00	0.13	0.10	1.0
Li Mg	3.26	−0.10	0.04	−0.02	−0.08	0.9
Mg Cd	3.29	−0.05	0.00	0.07	0.02	0.5
In Cd	3.35	0.06	−0.03	0.06	0.09	1.0
Ag Au	3.01	−0.03	0.00	−0.02	−0.05	0.7

ment of the positron pseudo wave function. In those cases where λ is about 1 or less a perturbation calculation of the positron pseudo wave function treating the pseudopotential difference to first order should be adequate. The full positron wave function may be obtained by modulating ψ^{pseudo} with the core function. In any event, the degree of localization of the positron around one sort of site or another is determined by the positron pseudopotential difference V_0, and it may be useful to take V_0 as a measure of the relative affinity of the positron for the two different sites in an alloy.

Experimental and theoretical evidence indicates that there are actual positron bound states around monovacancies in many metals. The possibility of positron bound states around impurities in metals will now be considered. The amount of lattice relaxation around an impurity in a metal is not known at present, but assuming that this is a small effect, an interstitial atom of the metal or an interstitial impurity atom should be repulsive to the positron. This is because the interstitial amounts to the insertion of an additional repulsive ion into the lattice. The situation is different for substitutional impurities, if the repulsive ion of the host is replaced by one much less repulsive, then a large attractive pseudopotential can result. Li, with its small core and valency of 1 has one of the largest positron affinities. It can be dissolved in small quantities in a number of metals. So as an impurity, it is a prime candidate for positron bound states.

Calculated positron pseudopotential differences for Li impurities in metals with increasing valency are presented in Table III. As expected there is a strong positron affinity for the Li impurity in all the cases except Li-Pb, where there is a large electron-charge-transfer contribution and a large $E^A_{\text{corr}} - E^B_{\text{corr}}$ balancing the zero-point energy difference. The magnitude of V_0 for Li-Ag is probably an overestimate since correlations between the positron and the $4d$ electrons of Ag have been neglected in the calculation of $E^A_{\text{corr}} - E^B_{\text{corr}}$. An inspection of the list of strength parameters indicates that there will probably be no bound state around a Li impurity in any of the metals studied since all the values of λ are significantly less than $\pi/2$. However, the large values of $|V_0|$ for Li in Ag, Mg, and Al suggest that a thermalized positron will sample more Li atoms than indicated by the atomic concentration, and this will be reflected in the results of positron-annihilation experiments. Since Li has probably the strongest positron affinity of any metallic impurity, it is safe to assert that there will not be positron bound states around the isolated impurities in dilute alloys.

IV. POSITRON-ANNIHILATION CORE RATE

This section is devoted to a discussion of a method by which information on the relative positron affinity for one component of an alloy may be deduced from experimental annihilation data and the role played by the positron pseudodensity in this respect. The measured annihilation rate and angular correlation curve for a positron annihilating in a binary alloy will reflect the way the thermalized positron is distributed between the two different sorts of sites, but it is not possible to deduce the way the positron is distributed directly from these measured quantities since the valence-electron distribution in an A cell of the alloy is different from the distribution in a cell of the pure A metal and so the electron distribution and the positron distribution both change with alloying, and the effects on the experimental data from one of these factors cannot be sorted out unambiguously from the effects of the other. However, the core electrons in simple metals are unaffected by alloying apart from small energy shifts. The atomiclike character of the valence electrons near the ions [the orthogonalized-plane-wave (OPW) "wiggles"] is also insensitive to alloying apart from a small change in amplitude. Furthermore the density of a thermalized positron in the region of an A atom core in the alloy, the other important factor affecting the annihilation characteristics in that region, is unchanged from the density in the core region in pure A metal apart from a slowly varying factor. This factor is the positron pseudodensity $|\psi^{\text{pseudo}}(\vec{r})|^2$, for the alloy. These arguments indicate that in an alloy that portion of the positron decay due to annihilation with core electrons and valence elec-

TABLE III. Mean atomic radius, three contributions to the positron pseudopotential difference, and the net pseudopotential difference V_0 for Li impurities in Ag, Mg, Al, and Pb. The square-well strength parameter is also listed.

A B	R_a(a.u.)	$E_0^A - E_0^B$ (Ry)	$E^A_{\text{corr}} - E^B_{\text{corr}}$ (Ry)	$E_f^A - E_f^B$ (Ry)	V_0 (Ry)	λ
Li Ag	3.01	−0.15	0.00	−0.05	−0.20	1.3
Li Mg	3.33	−0.09	0.04	−0.02	−0.07	0.9
Li Al	2.98	−0.19	0.09	−0.06	−0.16	1.2
Li Pb	3.65	−0.20	0.10	0.10	−0.00	0.0

trons with atomiclike features in an A cell will differ from that same portion of the rate for pure A metal only by the positron pseudodensity in the A core region in the alloy. This portion of the annihilation rate which has been called the core-annihilation rate, reflects strongly the distribution of the positron between different sorts of sites in an alloy.

It should be straightforward to deduce the core rate from experimental annihilation data. The rapid spatial variation of the core-electron wave functions and the "OPW wiggles" leads to high-momentum components in the positron-electron pair momentum distribution. These high-momentum components are manifested in the measured $2-\gamma$ angular correlation curve as a broad, roughly Gaussian, component extending far beyond the Fermi momentum. The ratio of this broad component in the measured pair momentum distribution to the total area should give the ratio of the core rate to the total measured annihilation rate.

The relation between the core rate for an AB alloy, the core rates for pure A and B metals, and the positron pseudodensity function in the alloy will now be developed. By analogy with the expression commonly used for the total annihilation rate,[19] the core rate for the alloy λ_c is written

$$\lambda_c = (\lambda_0/n_0)\int d\vec{r}\,\sigma(\vec{r})\,\rho_c(\vec{r})\,\xi(\rho_c(\vec{r})) \tag{16}$$

where λ_0 and n_0 are the total annihilation rate and the electron density at the position of the positron in singlet positronium. The positron density in the alloy is denoted by $\sigma(\vec{r})$ and $\rho_c(\vec{r})$ is the sum of the core-electron density and the density arising from atomiclike features of the valence electrons in the core region. The many-body enhancement of the rate due to the electron polarization cloud around the positron is accounted for by a factor ξ which is taken to be a function of ρ_c only. The core rates for the pure metals are given by

$$\lambda_c^x = (\lambda_0/n_0)\int d\vec{r}\,\sigma^x(\vec{r})\rho_c^x(\vec{r})\,\xi(\rho_c^x(\vec{r}))\,, \tag{17}$$

where again x refers to the species of atom either A or B.

The positron density in the alloy may be expressed in terms of the positron pseudodensity $\sigma^{\text{pseudo}}(\vec{r})$ using (12) and (13),

$$\sigma(\vec{r}) = [U_0^x(\vec{r}-\vec{R})]^2\sigma^{\text{pseudo}}(\vec{r})\ , \tag{18}$$

where $\vec{r}$ lies within an atomic cell of the alloy at $\vec{R}$ occupied by an atom of type x. To a very good approximation, $U_0^x(\vec{r})$ is the ground-state positron wave function in the core region and so

$$\sigma^x(\vec{r}) = [U_0^x(\vec{r}-\vec{R})]^2/\alpha^x\ . \tag{19}$$

Now using the slowly varying nature of the positron pseudodensity in the alloy, we find after some manipulation

$$\Delta\lambda_c = \frac{1-\sigma^A}{1+(\alpha^A/\alpha^B-1)\sigma^A}\ , \tag{20}$$

where $\Delta\lambda_c$, a reduced core rate, is given by

$$\Delta\lambda_c = (\lambda_c-\lambda_A)/(\lambda_B-\lambda_A)\ , \tag{21}$$

and the factors α^A and α^B defined earlier, in Sec. II, are the renormalization factors for the positron core functions in the alloy. The quantity σ^A appearing in (20) is the fraction of total positron pseudodensity in the A cells of the alloy and is given by

$$\sigma^A = \sum_{\vec{R}_A}\int_\Omega d\vec{r}\sigma^{\text{pseudo}}(\vec{r}-\vec{R}_A)\bigg/\int d\vec{r}\sigma^{\text{pseudo}}(\vec{r}), \tag{22}$$

where the summations are over the A sites in the alloy. An important feature of using the core rate and in particular (20) is that detailed computations of the overlap of the positron with core electrons are unnecessary and the difficult problem of estimating the enhancement of the rate due to positron-electron correlations is avoided. Both of these aspects are accounted for in the alloy core rate through the core rates for the two pure metals which may be deduced from experimental data on the pure metals.

If the valencies and the sizes of the ion cores of the constituents of the alloy are similar, then the ratio α^A/α^B is very nearly unity and the denominator in (20) is, therefore, also nearly unity. Furthermore if the positron pseudopotential difference V_0 is small in magnitude so that the positron shows no over-all preference for one sort of site or the other, then the positron pseudodensity would be uniform throughout the alloy. Inspection of (20) shows that the reduced core rate under these circumstances would decrease linearly from the value 1 for pure B to 0 for pure A as the alloy composition is varied assuming that there is no volume change on alloying. Any deviation from a straight line of the reduced core rate vs concentration plot would indicate a preference of the positron for either A sites or B sites. For a concave curve the positron pseudo wave functions would be larger at A sites than B sites as a result of $V_0 < 0$. In contrast a convex curve would indicate a positron affinity for B over A with $V_0 > 0$.

V. CONCLUSIONS

A simple picture of the thermalized positron distribution in an alloy has been presented. Through a factorization of the positron wave function the envelope of the positron density may be obtained in terms of a potential which has a convenient form and in many cases will be weak enough to allow the use of low-order perturbation theory. The strong repulsive potential when a positron approaches close to an ion and which leads to the depletion of positron density in these regions is accounted for by modulating the positron envelope with a prescribed positron core function. The term positron pseudo wave function is suggested for the envelope of the positron wave function and positron pseudopotential for the corresponding potential.

The positron pseudopotential difference between different sorts of sites in a binary alloy results from the preference of the positron for one sort of site or the other. This preference may conveniently be termed relative positron affinity, and the pseudopotential difference is a quantitative measure of this. A positron pseudopotential difference will lead to an enhancement of the pseudo wave function on the more attractive sites which in turn will result in the positron preferentially annihilating with the core electrons of one sort of atom in the alloy. To a fair approximation the contribution of core electrons to the total positron-annihilation rate in simple metals may be deduced from measurements of the positron lifetime and angular correlation curve. A measurement of this contribution, the core rate, for different alloy concentrations should yield directly information on the positron pseudo wave functions.

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