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POSITRON LIFETIMES IN SOLIDS FROM FIRST PRINCIPLES CALCULATIONS

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ABSTRACT

We present a first principles method for calculating positron lifetimes in solids, based on self-consistent calculations using the Linear Muffin-Tin Orbital method. Local density approximations are used for both electron-electron and electron-positron interactions. Results are presented for a variety of elemental metals and vacancies to demonstrate the reliability of this approach. Theoretical calculations of positron lifetimes can be used to interpret experimental data. As an example of this, we interpret our experimental lifetime data for the oxide superconductor $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ using calculations based on this method.

INTRODUCTION

Positron lifetime experiments provide a powerful probe of the bulk and defect electronic structure of materials. The positrons are very sensitive to defects, particularly vacancies, due to the strong Coulomb repulsion with the atomic nuclei [1]. In spite of this sensitivity, it is often difficult to determine which defect or defects are responsible for the observed lifetime, or indeed if the lifetime is defect or bulk related. This problem could be resolved if theoretical calculations for the positron lifetimes could be performed for the bulk, undefected material and for the associated defects. In the past, such calculations have been attempted using either parameterized fits to experimental data or with overlapping atomic charge density calculations which take no account of the charge redistribution in the vicinity of a defect [2, 3, 4].

Here we present a new approach for calculating the lifetimes of bulk materials and defects. In this method, the self-consistent electron charge density is used as the starting point for the positron calculation, so the effects of charge rearrangement around a defect are explicitly included. All electron-electron and electron-positron interactions are treated through local density approximations, which are obtained directly from electron-gas many-body calculations.

In contrast to many previous approaches, there is no fitting to experimental data in this method, and so it constitutes a first principles theory for calculating positron lifetimes in materials.

The method is outlined in the next section. Following that, we discuss the results of calculations on several elemental metals, where the bulk lifetime is well characterized experimentally. These calculations serve to demonstrate the accuracy and reliability of this approach. Results of lifetime calculations on the oxide superconductor $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ are then presented and compared with our experimental lifetime measurements. We conclude that the theoretical calculations are crucially important in interpreting the lifetime data in this system.

METHOD

The positron annihilation rate, λ , the inverse of the lifetime τ , is given by the equation [5, 6]

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

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 annihilation rate. In order to determine the lifetime, we must first calculate the three quantities n^- , n^+ and Γ . The electron charge density, n^- , is obtained from a self-consistent electronic structure calculation. In the results presented here, the Linear Muffin-Tin Orbital (LMTO) method [7] has been used. The electron-electron interactions are treated through the local density approximation (LDA) to density functional theory [8]. The positron charge density, n^+ , is found by calculating the positron wavefunction. Since the positron thermalizes rapidly upon entering the solid, it generally annihilates from the lowest accessible energy state. We can therefore use a variational approach to solve the positron Schrodinger equation and use the lowest energy positron wavefunction to construct n^+ . The positron Schrodinger equation,

$$\left[-1/2\nabla^2 - V_{\text{ion}}(\mathbf{r}) - V_{\text{Hartree}}(\mathbf{r}) + V_{\text{epcorr}}(n(\mathbf{r})) \right] \psi^+ = E^+ \psi^+ \quad (2)$$

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_{epcorr} . The ionic and Hartree terms are identical to those used in the electronic calculation, with a sign change due to the positive charge on the positron, and the Hartree term is calculated from the self-consistent electron charge density, n^- . V_{epcorr} is obtained from a local density approximation, derived from a two-component density functional theory [5, 6]. Such approximations have been highly successful in electronic structure calculations, and should, if anything, be even better in this case since the electron charge density is generally slowly varying in the interstitial region where the positron charge is primarily located. V_{epcorr} has been calculated for the homogeneous electron gas at various electron charge densities by Arponen and Pajanne [9]. We have

used a single functional form to obtain a fit to their results across the entire range of physically relevant charge densities:

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

where $(4\pi/3)r_s^3 n = 1$ and Rydberg units have been used.

The electron and positron charge densities can, in principle, be calculated exactly within density functional theory. This is not the case for the enhancement factor, Γ , which depends on the excitation properties of the electron gas. In spite of this, a local density approximation to Γ should be a reasonably good approximation in this case, in view of the slowly varying nature of the electron charge density in the interstitial region. We use the following expression, which is fitted to the free electron gas calculations of Lantto [5].

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

Density functional theory demands that the full electron charge density, n^- , be used in the calculation of V_{pcorr} . In the calculation of the enhancement factor, however, it is unlikely that the tightly bound core electrons will respond in the same way as the more polarizable valence electrons. This suggests that Γ may be different for the core and valence electrons. We have considered two approximations for the core contribution to annihilation. The first consists of the direct application of Eq. (1), with the full charge density used in the calculation of Γ . In the second approach, the less polarizable core is treated in the independent particle model (IPM), and only the valence electron charge density is included in the calculation of the enhancement. The annihilation rate is then given by

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

In general, we have found that the second approximation (IPM core plus enhanced valence) gives slightly better agreement with experiment for the elemental metals, so this approximation is used throughout the rest of this paper.

The method described here is a first principles approach for calculating the positron lifetimes of solids. No assumptions are made about the electron charge density or the positron wavefunction – both are calculated directly from first principles, and there is no fitting to experimental data. Further details of this method are given in Ref. [10].

ELEMENTAL METALS

In order to confirm the accuracy of this approach, a large number of lifetime calculations were carried out for elemental metals for which the bulk lifetime is well characterized experimentally. In addition, the positron lifetimes for monovacancies in a number of elemental metals were also calculated. The results are plotted in figure 1. The agreement with experiment is very good in

Figure 1: Plot of theoretical lifetimes against experimental lifetimes for a number of elemental metals and metallic monovacancies. Points lying on the diagonal line indicate exact agreement with experiment. Lifetimes are in picoseconds.

all cases. Note that this plot covers a wide range of systems, from the free-electron-like alkali metals through the transition metals with their more localized d-orbitals, and even includes the rare earth gadolinium. The same treatment of electron-positron interaction is used in all cases, so we do not need different forms for the enhancement of the s-p, the d and the f valence electrons. The density dependence of Γ leads naturally to different enhancements on the different orbitals. In multi-atom unit cell calculations, the same effect leads to different enhancements on different atomic sites, but the functional form of the enhancement factor remains unchanged. These results are discussed in more detail in Ref. [10].

LIFETIMES IN $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ (BKBO)

Experimental lifetime data [11] for two BKBO samples, $x = 0.4, 0.5$, are shown in figure 2. Lifetime values are in the range of 210–250 ps, and show a significant variation both with temperature and with aging. These variations can be readily explained in terms of defects in the material; variations in the lifetime with temperature frequently come about through competition between vacancy sites which can trap the positron before annihilation. At lower

temperatures, the positron has little thermal energy and can be trapped and annihilate in a shallow defect trap. At higher temperatures, the positron has more thermal energy, so it can escape the shallow trap and subsequently annihilate in a deeper trap. This mechanism generally gives rise to an increase in lifetime with temperature, since the deeper trap, which is relatively more attractive to positrons, is therefore less attractive to the negatively charged electrons, so the electron-positron overlap, and hence the annihilation rate, is reduced. The aging effect is also most likely associated with defects, although in this case the lifetime can either go up or down with time, depending on which defects are annealed or created during the aging process.

Theoretical calculations [12] of the lifetimes are indicated in the bars on the right hand side of figure 2. The size of the bars for the bulk and metal vacancy calculations indicate the range of lifetimes with potassium concentration varying from $x = 0$ to $x = 1$. The experimental lifetimes are much longer than the bulk lifetimes of 168-193 ps, but are in a range which is comparable to the lifetimes associated with defects, such as oxygen and metal atom vacancies. These defect calculations are carried out as supercells containing one vacancy, in an undistorted unit cell. For both samples, the high temperature data tends towards the calculated lifetime for the Ba/K vacancy, which has a lifetime of 248 ps, almost independent of the K concentration. This suggests that this defect is responsible for the trapping at higher temperatures, and that the lower temperature lifetimes are associated with shallower traps, which may be due to Bi vacancies, or some more complicated defect structure which has not been considered here.

The oxygen vacancies and the metal atom vacancies behave in a very different way. The metal vacancies tend to trap the positron, localizing its wavefunction very strongly in the vicinity of the defect. The oxygen vacancy, on the other hand, has only a minor effect on the positron wavefunction, and so does not lead to any significant trapping. This is illustrated in figure 3, where we plot the change in the positron wavefunction on all the neighboring sites when a vacancy is introduced. The introduction of a metal atom vacancy leads to large changes in the positron on all sites, as indicated by the shaded bars on the left hand side of the plot. By comparison, the changes introduced by the oxygen vacancy are very small, so the positron wavefunction is hardly affected by these defects. The calculated lifetime, however, will increase with the presence of oxygen vacancies, since there is now less charge density in the vacancy region, so the electron-positron overlap, and hence the annihilation rate, will be reduced. These vacancies can therefore increase the lifetime to values higher than the bulk lifetime without trapping the positron.

The electrostatic potential of the crystal favors a negative ion at the oxygen site, so an oxygen vacancy will naturally tend to attract electrons and repel positrons. This effect explains the insensitivity of the positron wavefunction to the oxygen vacancies. This also implies that the lifetimes will increase more or less linearly with the concentration of positron vacancies, so that when the number of vacancies becomes vanishingly small, the lifetime will tend towards the bulk value. This has been indicated schematically in figure 2 by the hatched region on the oxygen vacancy bar. The shaded part of this bar represents calculations for oxygen vacancy

Figure 2: Experimental lifetimes for $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$. Unaged data were taken on freshly prepared melt processed samples. Aged data were on the same samples after aging in air at room temperature for about one year. The bars on the right hand side indicate the lifetimes calculated theoretically for the bulk and vacancy defects, with potassium concentrations ranging from $x = 0$ to $x = 1$.

concentrations ranging from 1/6 to 1/3, and K concentrations varying from $x = 0$ to $x = 1$.

The right hand side of Figure 3 shows the change in the positron wavefunction on the vacancy site itself, compared with the wavefunction distribution for the bulk case. The change on the bismuth site is particularly dramatic. This is caused by the fact that the bismuth site is the least attractive site for the positron in the bulk case. The change on the oxygen vacancy site appears to be large, but this is produced by small changes on much larger atomic sites, and so has a much smaller overall effect on the lifetime than comparably sized changes on the potassium and barium sites.

CONCLUSIONS

We have described a new first principles approach for calculating the positron lifetimes of solids. The accuracy of this approach has been demonstrated by calculations on the elemental metals and monovacancies. Calculations of the positron lifetime in pure and defected BKBO have

Figure 3: Change in positron charge density on the various atomic sites when vacancies are created. The four bars on the right hand side of the graph show the increase in positron density on the vacancy compared with the density on that site in a bulk calculation. The sets of bars on the left hand side show the change in the density induced on the neighboring atomic sites when a vacancy of a given type is created. For example, the horizontally striped bar shows the change in the positron density on all the other atoms when a vacancy is created on one of the barium sites.

been used to analyse the experimental lifetime data of Ref. [11]. The calculations confirm that the observed lifetimes are defect related and lead to the identification of the K/Ba vacancy as the source the observed lifetime at high temperatures. The combination of experiment and theory has provided a detailed analysis of the nature of the defects in the material. The oxygen vacancies can increase the lifetime without significantly modifying the positron wavefunction. This effect is likely to be found in many other oxides.

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