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On positron annihilation in the superconducting cuprates

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Abstract. We consider a number of pertinent issues concerning high-T_c superconductors which could usefully be addressed by positron annihilation studies. Using a theory developed for binary random alloys, we explore the possibility of positron localisation in the superconducting cuprates.

1. Introduction

In spite of a monumental research effort the nature of pairing in the recently discovered high-temperature superconductors remains a mystery [1]. In this introduction, we wish to draw attention to a number of pertinent issues which could be usefully addressed by positron annihilation studies.

As is well known, lifetime measurements of implanted positrons made major contributions to the understanding of vacancies in metals [2]. Not only are such experiments able to detect the presence of monovacancies, by resolving an extra long-lifetime component when such vacancies are formed, but also they are unique tools for investigating the formation of vacancy clusters with annealing. Since oxygen vacancies appear to play an intriguing role in determining the superconducting properties of the $YBa_2Cu_3O_y$ cuprates [3], it is natural to try to study them by the above well tried method of positron annihilation lifetime and Doppler broadening energy spectra measurements. Indeed, there are many reports in the literature already of experimental efforts in these directions [4–6]. However, such studies will be able to monitor the presence and distribution of oxygen vacancies only if they are able to enhance the lifetime of an implanted positron by localising it. In order to aid the interpretation of the rapidly accumulating experimental data, we have studied this question of localisation theoretically. We shall present our results in § 2.

Another important feature of the new cuprate superconductors is that they appear to be near a metal–insulator transition. Under these circumstances there is a particular significance attached to the existence and nature of the Fermi surface in the normal state. Given the short mean free path even in the most metallic samples there is little hope of 'seeing' the Fermi surface of these materials, even if it exists, with any other probe than

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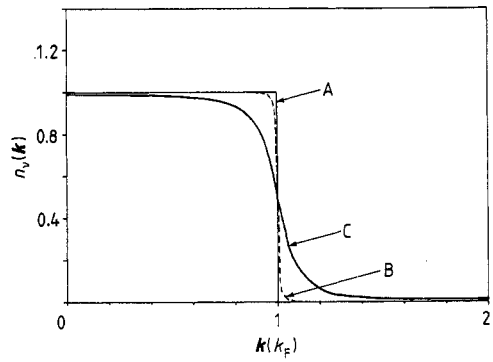

Figure 1. The electron momentum distribution $n_\nu(\boldsymbol{k})$ at $T = 0$: curve A, $\Delta_0 = 0$, $\xi_0 = \infty$; curve B, $\Delta_0 = 0.02E_F$ (here the Fermi energy $E_F = k_F^2 = 1$), $\xi_0 = 64$; curve C, $\Delta_0 = 0.2E_F$, $\xi_0 = 2.2$. For a conventional BCS superconductor with $\Delta_0 = 0.0002E_F$ and $\xi_0 = 3535$ the electron momentum distribution follows closely curve A.

two-dimensional angular correlation of annihilation radiation (2D ACAR) [7]. Indeed there is a lively interest already in doing this [8, 9]. However, again, to interpret these experiments, one will need a good understanding of the circumstances under which the positrons are not trapped but are in extended states.

Finally, we wish to note the interesting possibility that, in these materials, features of the superconducting state itself can be observed by measuring the electron momentum distribution function $n_\nu(\boldsymbol{k})$ in 2D ACAR experiments.

Let us recall that at $T = 0$ the electron momentum distribution, in the Hartree–Fock–Gorkov (BCS) approximation is given by [10]

$$n_\nu(\boldsymbol{k}) = \tfrac{1}{2}(1 - \tilde{\varepsilon}_{k,\nu}/\sqrt{\tilde{\varepsilon}_{k,\nu}^2 + \Delta_0^2}) = |v_{k,\nu}|^2 \tag{1}$$

where $\tilde{\varepsilon}_{k,\nu}$ is the normal-state quasi-particle energy measured from the chemical potential μ, Δ_0 is the superconducting gap at $T = 0$ and $|v_{k,\nu}|^2$ is the probability that the state labelled by the wavevector $\boldsymbol{k}$ and band index ν is occupied by a particle. In figure 1, we give a schematic picture of $n_\nu(\boldsymbol{k})$. Evidently in the superconducting state there is no sharp (Luttinger) cut-off at k_F (the Fermi momentum). In fact, $n_\nu(\boldsymbol{k})$ crosses the Fermi surface with a finite slope

$$\nabla_k n_\nu(\boldsymbol{k})|_{k_F} = -\hbar v_F(k)/2\Delta_0 = -(\pi/2)\xi_0 \tag{2}$$

where the zero-temperature coherence length ξ_0 is defined by the usual formula

$$\xi_0 = \hbar v_F(k)/\pi\Delta_0. \tag{3}$$

In conventional superconductors, ξ_0 is large (about 1000 Å) and the drop of $n_\nu(\boldsymbol{k})$ across the Fermi surface is too sharp to be observable. The point that we wish to make about the new high-temperature superconductors is that, for these materials, ξ_0 appears to be quite small (about 10–15 Å, of the order of the lattice parameter) and hence the width of the drop of $n_\nu(\boldsymbol{k})$ at $\boldsymbol{k}_F$ is a substantial fraction of the linear dimension of the Brillouin zone. Thus it should be detectable.

Moreover, at finite temperatures,

$$n_\nu(\boldsymbol{k}) = \tfrac{1}{2}[1 - (\tilde{\varepsilon}_{k,\nu}/E_{k,\nu})\tanh(\tfrac{1}{2}\beta E_{k,\nu})] \tag{4}$$

where $\beta = 1/k_B T$, and the quasi-particle energy $E_{k,\nu} = \sqrt{\tilde{\varepsilon}_{k,\nu}^2 + \Delta^2(T)}$. Consequently,

$$\nabla_k n_\nu(\boldsymbol{k})|_{k_F} = -(\pi/2)\xi_0\{\tanh[\Delta(T)/2k_B T]/(\Delta(T)/\Delta_0)\}. \tag{5}$$

Interestingly, the quantity in the curly brackets above does not vary much for the BCS superconductors. Furthermore, as $T \to T_c$, it goes to $\Delta_0/2k_B T_c$:

$$\nabla_k n_\nu(\boldsymbol{k})|_{k_F, T=T_c} = -(\pi/2)\xi_0\,\tfrac{1}{4}(2\Delta_0/k_B T_c). \tag{6}$$

For a BCS superconductor, $2\Delta_0/k_B T_c = 3.5$ and hence the above limit is consistent with

the suggestion that $\nabla_k n_\nu(\boldsymbol{k})|_{k_F}$ does not change much in the superconducting state. However, for the ceramic superconductors, $2\Delta_0/k_B T_c$ appears to be significantly different from the BCS value of 3.5. In fact, $2\Delta_0/k_B T_c$ has been reported to be as high as 8. Evidently, for such large values, equation (6) implies a change in $\nabla_k n_\nu(\boldsymbol{k})|_{k_F}$ by a factor of 2 as the temperature rises from $T = 0$ to $T = T_c$.

2. Do oxygen vacancies trap positrons in the superconducting cuprates?

Clearly, the answer to this question is crucial to the interpretation of the above experiments. No trapping is good news for the Fermi surface studies, but it means that oxygen vacancies are difficult to detect. On the contrary, if positrons are easily localised, and hence the vacancies can be readily detected, the Fermi surface work becomes problematic. Given this situation, our principal aim is to investigate whether or not the positron can become localised by the oxygen vacancy.

The question of positron localisation by oxygen vacancies is not as straightforward as that for vacancies in metals. It has to do with the fact that oxygen is a negative ion (O^{2-}) which for the positron at a distance is strongly attractive. Thus, while the lack of a positive nuclei at the centre of a vacancy is attractive for a positron, the competing attraction of the more numerous negative ions elsewhere may prevent the vacancy from binding the positron. To explore the validity of this observation, we shall regard the oxygen atoms and the vacancies in our material as two components of a more or less random alloy and use the principles governing the localisation of positrons in binary alloys. A theory of the conditions necessary for positron trapping in such systems has been developed by Szotek *et al* [11] and we shall adopt their main results as the basis for our discussion.

To state these results succinctly, consider a lattice of A and B sites and assume that the positron hops from site to site with an amplitude W_p, the band width, and that it has energy E_A at an A site and E_B at a B site. For many purposes the object of interest is the energy eigenvalue spectra for the positron averaged over all possible arrangements of the A and B sites. As is now well established [12–14] the coherent potential approximation (CPA) is a reliable way of dealing with such averaged spectra. For the above model a simple consequence of the CPA is that for $\Delta E = E_B - E_A \ll W_p$ the random A–B alloy has a single, fairly well defined band intermediate in energy between the corresponding pure A and pure B bands while, in the opposite case where $\Delta E = E_B - E_A \gg W_p$, we are in the split-band regime. Under this latter circumstance there are two bands well separated in energy. The state corresponding to one of these is such that it has large amplitudes on the A sites and small amplitudes on the B sites. The states which make up the other band imply that our particle spends most of its 'time' on the B site. As was stressed by Szotek *et al* [11] the implication of the above general prediction of the CPA for a positron is that for $\Delta E \gg W_p$ it will be more or less trapped at an A site and will annihilate preferentially with the electrons which form the electron density at the A sites.

For the reader not familiar with the large number of explicit calculations which support the general validity of the CPA for describing electrons, and therefore positrons, on a disordered lattice we offer another simpler and yet very powerful argument. Consider a positron at an A site with energy E_A. Such a state is not an eigenstate of the Hamiltonian with hopping. Indeed the positron will have a time $\delta t = \hbar/W_p$ to make a hop to a neighbouring, let us say, B site. During this time the energy need not be

conserved. In fact, its uncertainty is $\delta E = \hbar/\delta t = W_p$. Clearly, if $\delta E = W_p \gg E_B - E_A$, the hopping can be completed and the positron will propagate through the lattice in a single effective band. However, when $\delta E = W_p \ll E_B - E_A$ the hopping cannot be completed and the positron will have to find another A site if it is to move. Hence, there will be a band of states which correspond to the propagation of the positron through the lattice, visiting only the A sites. Naturally, there will be another band of states with amplitudes on the B sites only. Evidently, neither the A nor the B sites form a regular lattice and hence the states comprising the above bands will not be characterized by a definite crystal momenta $\boldsymbol{k}$. In short, they will be smeared by the disorder in both $\boldsymbol{k}$ and E. Obviously, the above picture of the positron band structure is the same as provided by the CPA.

The next step in our argument is to identify the A and B sites of the above discussion with oxygen atoms and vacancies in the $YBa_2Cu_3O_{6+x}$ compounds (x changes between 0 and 1). We pick a chain oxygen, O^{III}, in $YBa_2Cu_3O_7$ compound to be B, and its absence, V^{III}, to be A (see [15] for details). Thus $YBa_2Cu_3O_6$ is a pure 'vacancy' compound and $YBa_2Cu_3O_7$ is the pure 'oxygen' system. Hence, the compounds for intermediate values of x may be regarded as alloys of oxygen atoms and vacancies on the sublattice composed of III sites.

Given the above model, we can determine the site energies $E_B = E_{O^{III}}$ and $E_A = E_{V^{III}}$ by calculating the low-lying energy eigenstates of a positron in the two pure compounds, $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$, and locating the midpoints of the lowest bands. For this we have performed the separate LMTO ASA band-structure calculations for $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$ compounds, with the positron potentials constructed on the basis of the self-consistent electronic charge distributions obtained using the LMTO ASA method [15]. Surprisingly, the $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$ positron bands are very close. Taking $\delta E = E_{O^{III}} - E_{V^{III}}$ to be the difference between the bottom of the bands at the Γ point we find that $\delta E = 0.242$ eV. As we have argued above, this is to be compared with the band width W_p. We find the bands to be very anisotropic; however, the band widths for various possible symmetry directions of the simple tetragonal structure are very much the same for both compounds. In the language of tight-binding Hamiltonians this means that there is no off-diagonal randomness. Consequently, our arguments apply without modification. Thus comparing δE with the band widths in directions Γ–X, Γ–M (basal plane) and Γ–Z (c axis) we conclude that, while the positron may not be able to move in the Γ–Z direction ($\delta E \gg W_p^{\Gamma-Z} \simeq 0.1$ eV), it will not be trapped by vacancies in the plane ($\delta E \ll W_p^{\Gamma-X} \simeq 2.0$ eV and $\delta E \ll W_p^{\Gamma-M} \simeq 3.5$ eV).

In short, the realistic calculations of the positron band structures in $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$ strongly suggest that oxygen vacancies do not localise positrons in these compounds. This may be considered to be a consequence of the fact that the overall repulsion of positrons by the nuclei and attraction by the electrons of negative ions effectively cancel.

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