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Calculation of the angular correlation of the positron annihilation radiation in $\text{YBa}_2\text{Cu}_3\text{O}_7$

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Abstract. The aim of this paper is to evaluate the two-dimensional angular correlation of the positron annihilation radiation (2D ACPAR) in $\text{YBa}_2\text{Cu}_3\text{O}_7$. The calculation is performed in the independent-particle model using as electronic wavefunctions the molecular orbitals from a cluster calculation and a variational wavefunction for the positron. The anisotropic part of the 2D ACPAR and the folded distribution related to the theorem of Lock, Crisp and West are compared with experimental results.

1. Introduction

Since the discovery by Bednorz and Müller [1] of high-temperature superconductivity in perovskite-like oxides, many experimental techniques have been applied in order to study the electronic structure of the new superconductors [2].

Positron annihilation experiments (positron lifetime, Doppler broadening and one-dimensional (1D) or two-dimensional (2D) angular correlation of annihilation radiation (ACPAR)) are a useful probe of the electronic density distribution. Lifetime measurements have proved to be a sensitive method for studying vacancies in metals [3]. On the other hand, ACPAR experiments are more directly related to electronic momentum density [4].

2D ACPAR on $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ single crystals were performed by Hoffmann *et al* [5, 6] (along the [100], [110] and [210] crystal axes), Smedskjaer *et al* [7] (along the [001] crystal axis) and Haghghi *et al* [8] (along the [001] crystal axis). The former found good agreement when comparing their data with band-structure calculations [9], within the Lock, Crisp and West (LCW) [10] theorem framework. The results of the second group were found to be compatible with calculations of the electron–positron momentum distribution made by Bansil *et al* [11]. They calculated positron and electron momentum densities by the local-density approximation, and hence without the LCW assumption of constant positron wavefunction. Both conclude that a Fermi surface exists in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. On the other hand, the experimental results of Haghghi *et al* do not show the rapid changes in the LCW folded spectrum that would arise from singularities on the Fermi surface. They say that these changes may be hidden by an appreciable anisotropic component arising from the momentum distribution of the electron–positron pair. In fact, they explain the experimental anisotropies assuming a non-constant positron wavefunction and a localized LCAO MO electronic function. They consider only the

five antibonding wavefunctions obtained as a linear combination of the Cu 3d, O 2s and O 2p atomic orbitals with coefficients calculated by a least-squares fitting procedure with the experiment.

In La_2CuO_4 , 2D ACPAR measurements have been performed by Wachs *et al* [12] and Turchi *et al* [13], and the resulting experimental anisotropies are explained with a similar calculation to that in [8].

In this work we present calculations of the two- γ momentum distribution in $\text{YBa}_2\text{Cu}_3\text{O}_7$ for the four directions of integration where 2D ACPAR experimental results are known. The positron wavefunction was calculated as in [13] following the original idea of Chiba [14]. For the electronic wavefunction we also considered a LCAO MO picture, but with a slightly larger basis and coefficients calculated independently of the experimental results, using the iterative extended Hückel method (IEHM). To calculate the two-photon momentum density we used all the valence molecular orbitals. We discuss the need for this assumption and also the loss of information in the folding process related to the LCW theorem.

2. Method of calculation

2D ACPAR experiments measure the quantity

$$N(p_x, p_y) = \int_{-\infty}^{\infty} dp_z \rho_{2\gamma}(p_x, p_y, p_z) \quad (1)$$

where $\rho_{2\gamma}(\vec{p})$ is the two-photon momentum density, z is the direction joining the detectors, and x and y are the two axes in the perpendicular plane. As measurements are made on single crystals, one can choose z as being one of the crystalline axes.

The $N(p_x, p_y)$ experimental function is mostly isotropic. In order to amplify its anisotropic characteristics, a smooth isotropic function $f(p)$ is subtracted from it:

$$N_A(p_x, p_y) = N(p_x, p_y) - f(\sqrt{p_x^2 + p_y^2}). \quad (2)$$

This is the way in which Smedskjaer *et al* [7] and Haghighi *et al* [8] (for $\text{YBa}_2\text{Cu}_3\text{O}_7$) and Wachs and co-workers [11, 12] (for La_2CuO_4) presented their results.

Another way is to follow the spirit of the LCW theorem and to fold back the anisotropic function $N_A(p_x, p_y)$ into the projection of the first Brillouin zone in the plane perpendicular to the direction of integration:

$$N_F(k_x, k_y) = \sum_{\mathbf{G}} N_A(k_x + G_x, k_y + G_y) \quad (3)$$

where \mathbf{k} is a vector in the intersection of the first Brillouin zone and the plane perpendicular to the z axis, and \mathbf{G} is a reciprocal lattice vector in the same plane. This folding-back procedure for $\text{YBa}_2\text{Cu}_3\text{O}_7$ was performed by Hoffmann *et al* [5, 6], Smedskjaer *et al* [7] and Haghighi *et al* [8].

The conservation of momentum in the annihilation process allows us to relate $\rho_{2\gamma}(\mathbf{p})$ to the momentum of the electron-positron pair. In the independent-particle model (IPM) it can be written as

$$\rho_{2\gamma}(\mathbf{p}) = \text{constant} \sum_j^{\text{occ}} \left| \int d^3\mathbf{r} \exp\left(\frac{-i\mathbf{p} \cdot \mathbf{r}}{\hbar}\right) \psi_+(\mathbf{r}) \psi_j(\mathbf{r}) \right|^2 \quad (4)$$

where $\psi_+(\mathbf{r})$ is the positron wavefunction and $\psi_j(\mathbf{r})$ the wavefunction of the occupied electronic state j . To calculate $\rho_{2\gamma}(\mathbf{p})$ we had to model both wavefunctions.

For $YBa_2Cu_3O_{7-x}$, the narrowing of the momentum density with increase in the oxygen deficiency x [15], and the changes in the lifetime between orthorhombic ($x = 0$) and tetragonal samples ($x > 0.5$) [16, 17] show that the positron probes preferentially the electronic density in the basal plane. Theoretical calculations [13, 15, 18] also show that the probability of finding the positron is maximum in the basal plane. On the other hand, the valence electrons in these compounds form strong covalent bonds and are therefore localized in space. For this reason, single-particle LCAO MO wavefunctions must show the principal features of the charge distribution. We considered a cluster $(CuO_4)^{m-}$ formed by Cu(1) in the basal plane and its four nearest-neighbour oxygen atoms, two O(1) along the b axis and two O(4) along the c axis. The cluster charge $-m$ is used as a parameter, as it changes with the variable degree of covalency. The electronic function j is written as

$$\psi_j(\mathbf{r}) = \sum_i \sum_{nlm} C_{i,nlm}^j R_{nl}(|\mathbf{r} - \mathbf{R}_i|) Y_{lm}(\Omega_i) \quad (5)$$

where $R_{nl}(|\mathbf{r} - \mathbf{R}_i|)$ and $Y_{lm}(\Omega_i)$ are the radial and angular parts of the atomic function centred at atom i , nlm are the valence quantum numbers of the basis functions and $C_{i,nlm}^j$ are the expansion coefficients.

To calculate these coefficients we used the IEHM that takes into account electronic correlation in a mean-field way and also includes a Madelung contribution. The parameters needed for the IEHM are the ionization potentials and Slater orbital exponents for all the atomic orbitals considered: 3d, 4s and 4p for copper, and 2s and 2p for oxygen. The standard values for these parameters were used [19]. In this method the diagonal matrix elements of the Hamiltonian are assumed to depend quadratically on the total atomic charge and therefore some extra but also standard parameters are needed to allow for the iterative procedure. The Madelung correction takes into account the interaction of each electron with the electrostatic field arising from non-zero net charges in the other atoms of the cluster. The off-diagonal elements of the Hamiltonian are taken to be proportional to the overlap integral between the corresponding atomic orbitals. The total charge $-m$ of the cluster is also an input datum for the calculation. We tested the assumption of using the molecular orbital wavefunctions of the cluster $(CuO_4)^{m-}$ instead of periodic functions by making calculations in chains with the unit-cell formula CuO_3 (one basal Cu(1), one O(1) and two O(4)) and the same approximations for the Hamiltonian. We observed that taking into account the periodicity does not change the symmetry of the occupied states.

When the positron penetrates into the sample, it loses energy rapidly (in a few picoseconds) by ionization, creation of electron-hole pairs or interaction with phonons [4]. For this reason the positron in thermal equilibrium with the sample can be represented by a ground-state Bloch-type ($\mathbf{k} = \mathbf{0}$) wavefunction. The principal feature of the positron wavefunction in a primitive cell (i.e. repulsion by the positive cores) can be fairly well approximated by a variational wavefunction which has minimum probability at the core sites [12–14]:

$$\psi_+(\mathbf{r}) = N^{-1/2} \left(1 - \sum_i \exp(-\alpha_i |\mathbf{r} - \mathbf{R}_i|^2) \right) \quad (6)$$

where N is the normalization constant, \mathbf{R}_i the position of the i th ion and α_i the variational parameter that controls the affinity of the positron to the ion. These parameters should be found by minimizing the mean value of the positron energy. Their order of magnitude

is such that $\alpha_i d^2 \gg 1$, where d is a typical atomic distance. Near the atom i the positron wavefunction can be approximated as

$$\psi_+(\mathbf{r}) = N^{-1/2} [1 - \exp(-\alpha_i |\mathbf{r} - \mathbf{R}_i|^2)] \quad (7)$$

and, as we are dealing with a localized electronic function at a copper–oxygen cluster, the only α -values that we need are α_{Cu} and α_{O} . For FeO_4 , Chiba [14] found that $\alpha_{\text{Fe}} = 0.4713$ and $\alpha_{\text{O}} = 1.2470$ while Turchi *et al* [20] found that α_{Cu} varies between 0.605 and 0.647 and α_{O} between 1.326 and 1.437 for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($0 < x < 0.15$) and $\text{YBa}_2\text{Cu}_3\text{O}_7$ (α -values in units of a_0^{-2}). We tentatively used $\alpha_{\text{O}} = 1.2$ and $\alpha_{\text{Cu}} = 0.5$ regardless of the positron energy minimization, which could introduce only small variations. These small changes in the α -values do not modify the anisotropy of the momentum distribution but have the effect of broadening (or narrowing) the radial extension of $\rho_{2\gamma}(\mathbf{p})$.

Using these assumptions for electron (equation (5)) and positron (equation (7)) wavefunctions with the standard expansion of $\exp(-i\mathbf{p} \cdot \mathbf{r}/\hbar)$ in spherical harmonics [21], the function $\rho_{2\gamma}(\mathbf{p})$ can be written as

$$\rho_{2\gamma}(\mathbf{p}) = \text{constant} \sum_j^{\text{occ}} \left| \sum_{i,nl m} 4\pi C_{i,nl m}^j (-i)^l K_{i,nl}(p) Y_{lm}(\Omega_p) \exp\left(\frac{-i\mathbf{p} \cdot \mathbf{R}_i}{\hbar}\right) \right|^2 \quad (8)$$

where

$$K_{i,nl}(p) = \int_0^\infty R_{i,nl}(r_i) \psi_+(r_i) j_l\left(\frac{pr_i}{\hbar}\right) r_i^2 dr_i \quad (9)$$

with $r_i = |\mathbf{r} - \mathbf{R}_i|$ and j_l the spherical Bessel function of order l . To obtain $N(p_x, p_y)$ we integrated numerically $\rho_{2\gamma}(\mathbf{p})$ along p_z in a grid of 51 by 51 points with the p_x, p_y running from $-13 \times 10^{-3} mc$ to $13 \times 10^{-3} mc$ (where m is the mass of an electron and c is the velocity of light). The isotropic function $f(p)$ was chosen as a polynomial of sixth degree. The coefficients were found by a least-squares fitting with an annular average of the calculated 2D distribution. We averaged over a ring of width about $0.15 \times 10^{-3} mc$. The polynomial function has more adjustable parameters than for example a simple gaussian and therefore allows a better fit of the average distribution. On the other hand, it does not introduce spurious structure.

3. Results

We have used in this work the electronic wavefunctions calculated for a cluster $(\text{CuO}_4)^{m-}$. In the case of complete ionization the cluster should have $m = 6$, corresponding to Cu^{2+} and O^{2-} , but a more covalent bonding would give a smaller value for m . To study this effect we tried $m = 3$ and $m = 6$. In both calculations near the Fermi energy we found five antibonding MOS of similar character to those proposed in [8, 13]. In our case the contribution to the anisotropic function $N_A(p_x, p_y)$ arising from these orbitals is not the only important one; in other words, the contribution of the remaining MOS to $N(p_x, p_y)$ is not an isotropic gaussian-like function. Figure 1 plots the contribution to $N(p_x, p_y)$ from the occupied MOS excluding the five antibonding MOS near the Fermi level, which clearly shows some anisotropy. The calculation has been made assuming $m = 3$ and the direction of integration along [100]. We have obtained similar results for $m = 6$ and other directions of integration. For this reason we used all the valence MOS.

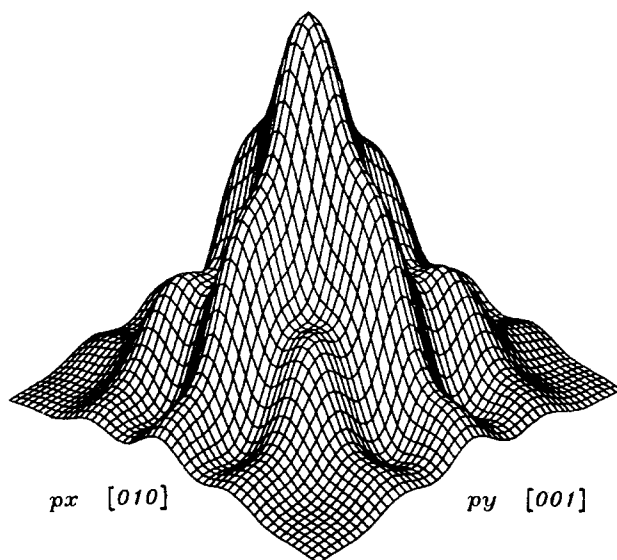


Figure 1. Contribution to the integrated momentum distribution $N(p_x, p_y)$ of all the occupied MOS, except the five antibonding MOS near the Fermi level, of a cluster $(CuO_4)^{3-}$. The direction of integration is the $[100]$ axis. The values of p_x and p_y range between $-13 \times 10^{-3} mc$ and $+13 \times 10^{-3} mc$.

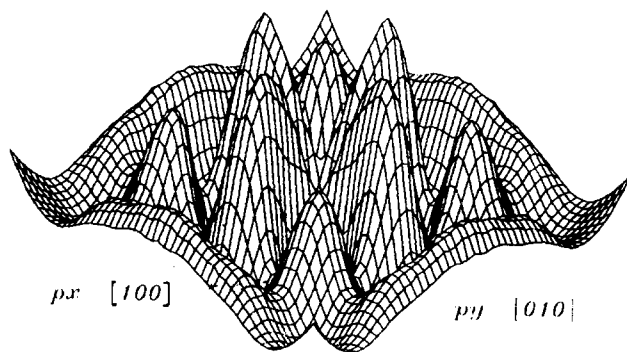


Figure 2. Anisotropic part N_A of the momentum distribution integrated along $[001]$ calculated using all the molecular orbitals of a cluster $(CuO_4)^{3-}$. This should be compared with figure 1(b) of [7]. The values of p_x and p_y range between $-13 \times 10^{-3} mc$ and $+13 \times 10^{-3} mc$.

Figure 2 shows $N_A(p_x, p_y)$ integrated in the $[001]$ direction for $m = 3$ and should be compared with figure 1 of [7]. We obtain four peaks at the corners and another four at the sides, the former being slightly more external. Although the different isotropic functions $f(p)$ do not introduce spurious structure, they give different relative heights for the existing peaks. This must be the reason for the differences between our calculations and the results of Smedskjaer *et al* [7] concerning the relative height of the peaks at corners and sides. For example our first choice was a gaussian surface but in that case we obtained a large central peak due to the small number of low p -values in

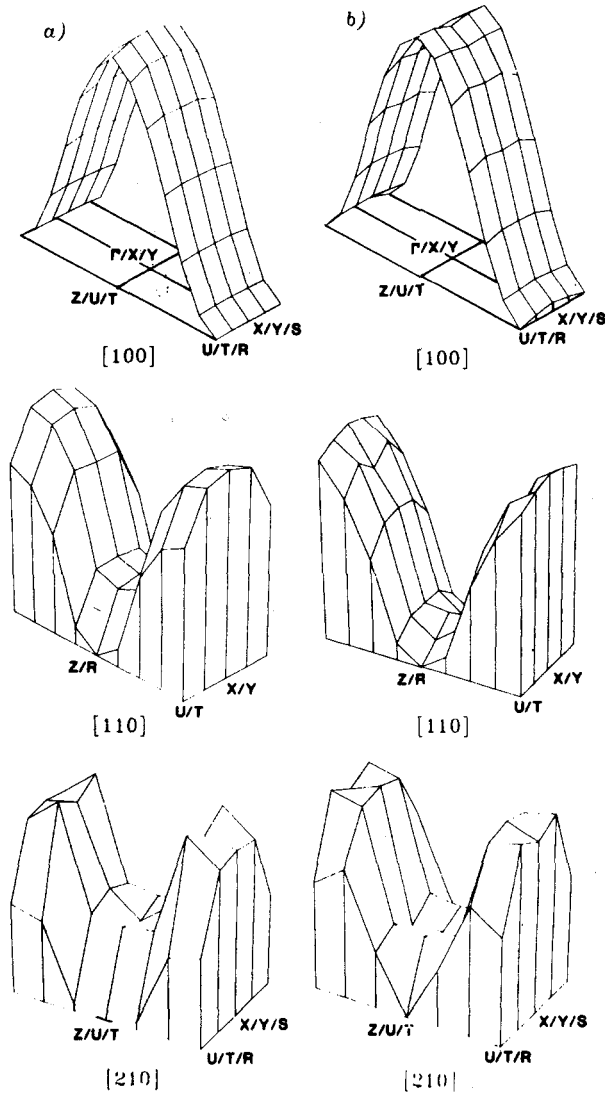


Figure 3. Folded momentum distribution N_F for three different directions of integration and two values of the cluster total charge: (a) $m = 3$; (b) $m = 6$. The integration directions are from top to bottom $[100]$, $[110]$ and $[210]$. This should be compared with figure 1(a) of [6].

the fitting procedure and that obscured the lateral peaks. The equivalent figure for $m = 6$ shows similar anisotropic features.

In order to compare our calculations with the results of Hoffmann *et al*, we folded our anisotropic distribution using the same procedure as they did. That is, as in [5, 6], we folded the anisotropic part of the momentum distribution instead of the total distribution, regardless of the physical meaning of this process. We calculated $N_F(k_x, k_y)$ for three different directions of integration: $[100]$, $[110]$ and $[210]$. In figures 3(a) and 3(b) we show our calculations for $m = 3$ and $m = 6$, respectively, and it is clear that both values of m reproduce the experimental results fairly well. The similarities between the

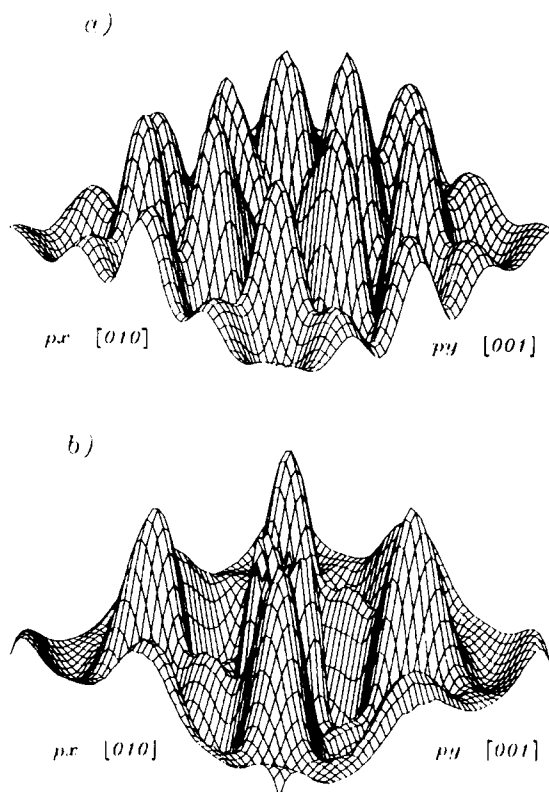


Figure 4. Anisotropic part N_A of the momentum distribution for the direction $[100]$ and two different cluster total charges: (a) $m = 3$; (b) $m = 6$. The folded counterpart of these anisotropic distributions are given at the top of figure 3. The values of p_x and p_y range between $-13 \times 10^{-3} mc$ and $+13 \times 10^{-3} mc$.

N_F functions for the two m -values is a consequence of the folding process, as the corresponding anisotropic functions are not so similar. For example in figure 4(a) and 4(b) we show N_A for $m = 3$ and $m = 6$, respectively, both integrated along $[100]$.

Independently of the existence or not of a Fermi surface our calculations reproduce the experimental results quite well when both are folded with the same procedure. The apparent differences arise owing to the sparsity of our mesh in figure 3. This appears for the following reason: using the cell parameters for $\text{YBa}_2\text{Cu}_3\text{O}_7$ (i.e. $a = b \approx 3.85 \text{ \AA}$ and $c \approx 11.7 \text{ \AA}$) it is clear that the size of the first Brillouin zone (in p units between 2.08 and $6.24 \times 10^{-3} mc$) is much smaller than the extension of the momentum density function (approximately $25 \times 10^{-3} mc$). In table 1 we show the size of the projection of the first Brillouin zone in the plane perpendicular to the integration direction, and the resultant size of the grid for the folded function $N_F(k_x, k_y)$.

4. Conclusions

We have calculated the anisotropic features of the 2D ACPAR for $\text{YBa}_2\text{Cu}_3\text{O}_7$ using LCAO MO electronic wavefunctions and a Bloch-type ($\mathbf{k} = 0$) positron wavefunction. We found

Table 1. Projection of the first Brillouin zone in the plane perpendicular to the direction of integration p_z . p_x and p_y are two directions in this plane; B_x and B_y are the length of the sides of the rectangular first-Brillouin-zone projection in units of $10^{-3} mc$. The last column shows the size of the remaining grid after the folding process.

| p_x | p_y | p_z | B_x | B_y | Size of the grid |
|---------------|-------|-------|-------|-------|------------------|
| [010] | [001] | [100] | 6.24 | 2.08 | 13×5 |
| $[1\bar{1}0]$ | [001] | [110] | 4.41 | 2.08 | 9×5 |
| $[1\bar{2}0]$ | [001] | [210] | 2.79 | 2.08 | 7×5 |

that not only is the anisotropy due to the MOS close to the Fermi energy but also the contribution of the lower levels is important. As can be seen in equation (4), each valence MO gives a positive contribution to the momentum distribution and is highly anisotropic. Nevertheless, for certain groups of MOS the anisotropic features cancel each other and they give a net almost-isotropic contribution to the total distribution. It is, however, in general impossible to know *a priori* which are those groups.

The anisotropic function N_A calculated along [001] approximates quite satisfactorily the experiments of Smedskjaer *et al* [7] and Haghghi *et al* [8]. We believe that the main difference between the distributions (i.e. the relative height of the peaks) is caused by differences in the choice of the isotropic function $f(p)$.

We also found good agreement between our calculations of the folded distribution along the axes [100], [110] and [210] and the experimental results. In this case, there is a loss of information due to the folding procedure, so that the results are less dependent on the parameters used in the calculation and, in particular, the cluster charge. Our aim was not to decide on the existence of a Fermi surface but to show that the qualitative features of the folded distribution are the same, therefore showing that our calculated wavefunctions represent the electronic distribution for $\text{YBa}_2\text{Cu}_3\text{O}_7$ fairly well. Our calculations also support the hypothesis that positrons mostly sample the chain region, as our clusters represent that part of the crystal.

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