Symmetry analysis of the electron wave functions in the antiferromagnetic phase of high-temperature superconductors

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An analysis of the symmetry of the wave functions of electrons in antiferromagnetic planes of CuO_2 high-temperature superconductors makes it possible to investigate the permissible electron states at characteristic points of the magnetic Brillouin zone. Interpretation of the results provides an opportunity for experimental determination of the nature of carriers in high-temperature superconducting materials, i.e., determination of whether the *p–d* hybridization or the "oxygen" model conserving the valence of copper is correct.

1. INTRODUCTION

In a recent paper[1] we proposed a transparent method for constructing irreducible double-valued corepresentations (IDCs) of the magnetic group of a two-sublattice antiferromagnet. The main applications considered in Ref. 1 were the specific properties of the electron states near the boundary of a magnetic Brillouin zone. In the present paper we use a group-theoretic approach to describe the electron states in the antiferromagnetic phase of high-temperature superconducting materials.

We consider a square antiferromagnetic ordered lattice of CuO_2 and concentrate on the high-symmetry points in the appropriate magnetic Brillouin zone, where the extrema of one-particle spectra are most likely to lie. We deduce the classification of the symmetrically permissible states and the selection rules for optical transitions. Unexpectedly significant information is shown to follow from constructing explicit bases of IDCs in terms of the atomic orbitals of copper and oxygen.

We show that different IDCs at the high-symmetry points of a magnetic Brillouin zone correspond to different concepts of the microscopic nature of the electron states. Therefore, it should be in principle possible to make a qualitative experimentally based choice between the competing models (see, for example, the reviews in Refs. 2–4) of an insulating antiferromagnetic phase of superconducting oxides.

2. CONSTRUCTION OF THE BASIS

In constructing exclusively the basis of an IDC at the points X and M of a magnetic Brillouin zone (Fig. 1) we must make sure that each magnetic IDC corresponds to a specific irreducible representation of the same equivalent nonmagnetic Brillouin zone. The elements of a magnetic IDC can be deduced from elements of the corresponding representations for an ordinary crystal by loading the latter with transformations in spin space, which are matrices $\mathbf{n}\boldsymbol{\sigma}$ and σ_0, in accordance with the rules given in Ref. 1. [Here, $\mathbf{n}$ is the antiferromagnetic vector, σ_0 is a unit matrix, $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ are the Pauli matrices.] The basis functions of the magnetic IDCs—spinors $\psi(\mathbf{r})$—can also be readily constructed from the basis functions $\varphi_i(\mathbf{r})$ of the representations of a nonmagnetic group. In fact, we have

$$\Psi_\pm(\mathbf{r}) = [(\sigma_0 \pm \mathbf{n}\boldsymbol{\sigma})\varphi_i(\mathbf{r}) + (\sigma_0 \mp \mathbf{n}\boldsymbol{\sigma})\varphi_j(\mathbf{r})]\begin{pmatrix}\alpha\\ \beta\end{pmatrix}. \tag{1}$$

Here, $\varphi_i(\mathbf{r})$ and $\varphi_j(\mathbf{r})$ are the basis functions of the representations whose elements are identical for operations weighted by the matrix σ_0 (group S in Ref. 1) and opposite in sign in the case of operations weighted by the matrix $\mathbf{n}\boldsymbol{\sigma}$ (operations involving $F = P/S$ in Ref. 1); Ψ_+ and Ψ_- are the wave functions of magnetic IDCs separated by an antiferromagnetic energy gap.

In future we shall always assume that the quantization axis of an IDC, the $\mathbf{z}$ axis, is directed along the vector $\mathbf{n}$. In this case we can use the simple relationship $\Psi_\pm = (\Psi_\mp)^T$, where T is the transportation operation.

We now find the explicit form of the electron wave functions of an antiferromagnet at the points X and M of the magnetic Brillouin zone of CuO_2.

Point *X*, center of the magnetic brillouin zone boundary

The symmetry group of the point X consists of rotation U_{2X} by 180° about the x axis (Fig. 1) and rotation U_{2Y} by 180° about the y axis, which is weighted by the matrix $\mathbf{n}\boldsymbol{\sigma}$. Translation by one antiferromagnetic lattice period along the direction y reverses the sign of the wave function, whereas translation along $\mathbf{x}$ leaves the sign invariant. The wave functions, which are even (e) and odd (o) relative to rotation U_{2X} in the basis of atomic orbitals of copper, deduced from Eq. (1), are

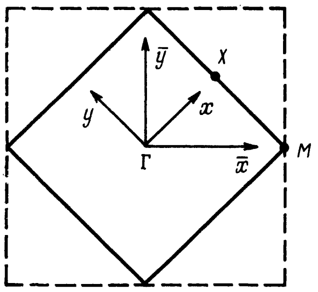

FIG. 1. Brillouin zones of an antiferromagnet (continuous line) and a normal metal (dashed line) with a square crystal lattice: Γ, M, and X are the characteristic (high-symmetry) points.

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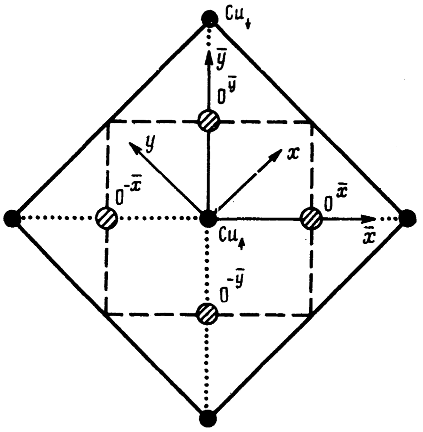

FIG. 2. Distribution of copper and oxygen atoms in an antiferromagnetic cell of CuO_2.

$$\Psi_+^{(e)}=(\Psi_-^{(e)})^T=\begin{pmatrix} |z\rangle\cos x\oplus i|x\rangle\sin x\oplus|y\rangle\sin 2y\cos x \\ |x\rangle\cos x\oplus i|z^2\rangle\sin x\oplus i|y\rangle\sin 2y\sin x\end{pmatrix}, \tag{2}$$

$$\Psi_+^{(0)}=(\Psi_-^{(0)})^T=\begin{pmatrix} i|d\rangle\sin x\oplus i|x\rangle\sin x\sin 2y\oplus|y\rangle\cos x \\ |d\rangle\cos x\oplus|x\rangle\cos x\sin 2y\oplus i|y\rangle\sin x\end{pmatrix}. \tag{3}$$

Here, the sign $\oplus$ denotes summation with coefficients which are certain functions of the coordinates and are invariant under the operation of the symmetry group P of the point X: $P=D_2$.

We consider the orbitals of copper $|d\rangle\sim\bar{x}^2-\bar{y}^2\sim xy$ and $|z^2\rangle\sim 2z^2-x^2-y^2$ and orbitals of oxygen $|p\rangle$:$\{|x\rangle\sim x,\ |y\rangle\sim y\}$. We ignore terms of the form $|d\rangle\sin 2y\cos x$, and $|d\rangle\sin 2y\sin x$; these transform in the same way as $|z^2\rangle\sin x$ and $|x\rangle\cos x$, which vanish at the copper atoms, because of an oscillating factor, i.e., they do not correspond to its orbitals.

It should be noted that the irreducible representations of Eq. (2) do not contain the $|d\rangle$ orbitals of copper, whereas the odd representations of Eq. (3) do not contain the $|z^2\rangle$ orbitals. The representation (3) corresponds to the p–d hybridized electrons, for example, in the case of the weak binding model and the average field approximation for an intrinsic antiferromagnet CuO_2. In the tight-binding model both edges (±) of the antiferromagnetic gap are again formed by the eigenstates of Eq. (3), but only the change in the population numbers of the d states admits both types of changes in the valence of copper: $Cu^{2+}\to Cu^{3+}$ and $Cu^{2++}\to Cu^{+}$. Another important case is that in which the state of Cu^{3+} is either not realized at all or it becomes a hole in the $|x^2\rangle$ state (which is the effect of the Hund rule—Ref. 3), whereas electrons still occupy the $|d\rangle$ states of copper. Then, the electron and hole states at the point X, which are the lowest on the energy scale, correspond to very different irreducible representations of Eqs. (3) and (2), and not to similar states of the (±) pairs of the representation of Eq. (2) or Eq. (3). These two band schemes have different optical properties, since in the latter case the dipole optical transition is forbidden.

Point *M*, corner of the magnetic brillouin zone

In the nonmagnetic case the space symmetry group of the point M contains the point group $P=D_4$ and translation by one period of an antiferromagnetic lattice $T_{x,y}$ which reverses the sign of the wave function. The group has four one-dimensional (M_1–M_4) and one two-dimensional (M_5) representations. The wave functions φ_i obtained in the basis of the d, z^2, and p orbitals corresponding to these representations are listed in Table I. Using Eq. (1), we can find all the IDCs of the magnetic group listed in the table of Ref. 1. They are the four doubly degenerate one-dimensional representations $\Psi^1_+=\Psi_{1,3}$, $\Psi^1_-=\Psi_{3,1}$ and $\Psi^2_+=\Psi_{2,4}$, $\Psi^2_-=\Psi_{4,2}$, separated by an energy gap, and also quadruply degenerate two-dimensional representation

$$\Psi^5_{\bar{x},\bar{y}}={}^1/_2[\Psi^5\mp(\Psi^5)^T].$$

Here

$$\Psi_{i,j}=\begin{pmatrix}\varphi_i\\ \varphi_j\end{pmatrix},\qquad \Psi_5=\begin{pmatrix}\varphi_5(x,y)\\ \varphi_5(y,x)\end{pmatrix},$$

φ_i ($i=1,\ldots,5$) represents the basis functions listed in the ith row of Table I; $\bar{x}=\frac{1}{2}(x-y)$, $\bar{y}=\frac{1}{2}(x+y)$ (Fig. 2).

As in the case of the point X, we ignore the wave functions of the $|p\rangle\sim|d\rangle(\sin 2y,\ \sin 2x)$, $|z^2\rangle(\sin 2x,\ \sin 2y)$, type, which have zero amplitude at the copper atoms.

The explicit form of the combinations of the d, z^2, and p orbitals of copper and oxygen located in an antiferromagnetic cell (Fig. 2), corresponding to the basis functions of the IDC at the point M, are given in Table II.

It is clear from Table II that only the representations Ψ^1_+ and Ψ^1_- include contributions from the $|d\rangle$ and $|z^2\rangle$ orbitals of copper. These representations correspond to the hybridized copper–oxygen energy band.

Another pair of states Ψ^2_+ and Ψ^2_- and the degenerate pair $\Psi^5_{\bar{x},\bar{y}}$ do not include contributions from the $|d\rangle$ and $|z^2\rangle$ orbitals of copper. We can assume that these states correspond to the "valence conservation" of copper. In the case of holes we are dealing with the "oxygen" model,[5] where the wave functions of carriers are constructed solely from the orbitals of oxygen. We can subsequently ignore the Ψ^2_+ and Ψ^2_- because they correspond to states with antibonding orbitals and these can represent only strongly excited states. The reason is that the wave functions of these states have zeros at the copper atoms, i.e., there is no overlap of the $|p\rangle$ oxygen orbitals at the copper atoms. In fact, in the coordinate space these states are the xy configurations plotted from the oxygen $|p\rangle$ orbitals, which is not justified from the energy point of view.

It therefore follows that the only manifestation of the oxygen model we are left with is the IDC $\Psi^5_{\bar{x},\bar{y}}$. The doubly degenerate level $\Psi^5_{\bar{x},\bar{y}}$ is the only state for which the concept of a particle (hole) moving only between the oxygen atoms without a change in the valence states of the Cu^{2+} ions is physically meaningful.

We therefore obtain the following two symmetry-allowed types of wave functions at the point M, which should be distinguishable experimentally:

1. A pair of hybridized wave functions Ψ^1_+, Ψ^1_- for electrons and holes. In this case an optical transition is dipole-forbidden.

2. An electron band Ψ^1_+ and a pair in contact at the point M within the hole bands $\Psi^5_{\bar{x},\bar{y}}$ (like holes at the point Γ

TABLE I.

i	M	Γ
1	$\vert a\rangle \cos x \cos y \oplus \vert d\rangle \sin x \sin y \oplus$ $\oplus (\vert x\rangle \sin x + \vert y\rangle \sin y)$	$a = s,\ z^2$
2	$\vert y\rangle \sin x \cos y - \vert x\rangle \sin y \cos x$	$dd' = xy\,(x^2 - y^2)$
3	$\vert a\rangle \sin x \sin y \oplus \vert d\rangle \cos x \cos y \oplus$ $\oplus (\vert x\rangle \sin y + \vert y\rangle \sin x)$	$d = xy$
4	$\vert x\rangle \sin x \cos y - \vert y\rangle \sin y \cos x$	$d' = x^2 - y^2$
5	$[y,\ x] \sin x \sin y + [x,\ y] \cos x \cos y$	$p = [x,\ y]$

Note. The basis functions of irreducible representations are given for the symmetry group of a square lattice at the corner of the Brillouin zone (point M) and for the corresponding representations of the group D_4, identical with representations in the center of the Brillouin zone (point Γ).

in semiconductors of the Si type). The interband optical transitions are allowed. The degeneracy of $\Psi^5_{\bar{x},\bar{y}}$ is either lifted by the spin–orbit interaction[1] or by orthorhombic distortions.

A very interesting but not very likely case can occur in any of the similar compounds. If the valence of ions such as copper is conserved under any variation, then both electrons and holes correspond to the $\Psi^5_{\bar{x},\bar{y}}$ representation. This possibility corresponds to a zero-gap semiconductor with a pointlike Fermi surface which is in contact with empty and filled energy bands.

3. CONCLUSIONS

We have derived allowed forms of the explicit one-particle wave functions at the high-symmetry points of a magnetic Brillouin zone. The results make it possible to determine experimentally the nature of the electron states both in high-temperature superconductors and in other antiferromagnets, such as NiO.

The current model theories usually describe the electron structure of superconducting oxides in terms of rigidly selected orbitals for atoms or clusters. Such wave functions can be determined rigorously only in the vicinity of the point Γ, where the influence of antiferromagnetism is insignificant. Moving from the point Γ to the boundary of the magnetic Brillouin zone and then along this boundary, we cannot know *a priori* which of the representations of the singular points X and M from Ref. 1 is appropriate. In any case at an arbitrary point in the magnetic Brillouin zone and on its boundary there is a mixture of all possible orbitals of copper and oxygen. Since all the energy parameters are comparable in magnitude, it is quite difficult to interpret the experimental data for an arbitrary point in the magnetic Brillouin zone, since these parameters can correspond to one or another Hamiltonian. However, our results show that at the high-symmetry points on the boundary of the magnetic Brillouin zone the one-electron wave functions corresponding to different irreducible representations of the magnetic symmetry group are qualitatively different. At these points the various hypotheses on the electron structure assume a pure symmetry-distinguishable form.

The following hypotheses are currently in competition: these hypotheses are put forward in Refs. 5–11 and they differ in the nature of holes postulating either oxygen p states or hybridized p–d orbitals of oxygen and copper. The corresponding insulating gap can be interpreted as the "charge-transfer" gap[7,10,11] between copper and oxygen or as the Mott–Hubbard gap in an effective one-band model.[8,9]

The hypothesis that holes move only between the oxygen atoms (Ref. 6, see also Refs. 3 and 7) can be proved by detecting, at the point M, a 2×2 multiple degenerate level $\Psi^5_{\bar{x},\bar{y}}$. This assumption corresponds also to the even IDCs at the point X, but in this case in addition to the oxygen orbitals we can include the filled $|x^2\rangle$ orbital of copper, which is interesting to compare with the case of a partly filled $|z^2\rangle$ orbital in La_2NiO_4.

The hypothesis of a gap of the charge transfer type corresponds to an optical transition allowed at the point M, but forbidden at the point X. Opposite selection rules for the dipole optical transition apply to the Mott–Hubbard antiferromagnetic gap in the one-band model.[8,9]

A direct observation of the properties of electrons at the selected points of the magnetic Brillouin zone can be carried out using the x-ray photoelectron spectroscopy (XPS) with angular resolution, the effectiveness of which has already been tested by investigations of the metallic phase.[12] Optical

TABLE II.

	$Cu_\uparrow$	$Cu_\downarrow$	$O^{\pm\bar{x}}$	$O^{\pm\bar{y}}$
Ψ_+^1	$\vert d,\ \downarrow\rangle \oplus \vert z^2,\ \uparrow\rangle$	$\vert d,\ \uparrow\rangle \oplus \vert z^2,\ \downarrow\rangle$	$\vert \pm\bar{x},\ \uparrow + \downarrow\rangle$	$\vert \pm\bar{y},\ \uparrow - \downarrow\rangle$
Ψ_+^2	0	0	$\vert \pm\bar{y},\ \uparrow + \downarrow\rangle$	$\vert \pm\bar{x},\ \uparrow - \downarrow\rangle$
$\Psi_{\bar{y}}^5,$	0	0	$\vert \alpha\bar{y},\ \uparrow + \downarrow\rangle,$	$\vert \beta\bar{y},\ \uparrow - \downarrow\rangle,$
$\Psi_{\bar{x}}^5$			$\vert \beta\bar{x},\ \uparrow + \downarrow\rangle$	$\vert \alpha\bar{x},\ \uparrow - \downarrow\rangle$

Note. The combinations of the z^2, d, and p orbitals of copper $Cu_\uparrow$, $Cu_\downarrow$, and of oxygen $O^{\pm\bar{x}}$, $O^{\pm\bar{y}}$ (Fig. 2) correspond to irreducible representations Ψ^1_+, Ψ^2_+, and $\Psi^5_{\bar{x},\bar{y}}$ for the magnetic group at the point M. The basis functions corresponding to the representations Ψ^1_-, Ψ^2_- are obtained from the functions Ψ^1_+, Ψ^2_+ by the transposition operation; $|\uparrow\rangle = \binom{1}{0}$, $|\downarrow\rangle = \binom{0}{1}$.

measurements can give information only near the minimum of the energy gap, which is not known *a priori* and which occurs at the point X or at the point M.

After some generalizations the results can be applied also to the electronic properties of other antiferromagnetic oxides such as NiO (Ref. 13).

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