Electron spectrum and insulator transition in oxide layers

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A model for the electron spectrum of quasi-2D substances with carriers of oxygen origin is proposed.

One of the sharpest contradictions in the current interpretation of the nature of high-temperature superconductors is that band calculations[1,2] indicate that La_2CuO_4 and $YBa_2Cu_3O_6$ should be metals, while experimentally they exhibit insulating properties.[3] The same contradiction is seen in the model of p-d hybridization, which illustrates the band calculations: The width of the conduction band responsible for the kinetic properties is of the same order of magnitude as the band in which the spins of the copper atoms are localized (according to neutron experiments).

One can avoid these difficulties by assuming that the charge-carrier band arises from a direct overlap of oxygen orbitals. The electron states at the copper should then be assumed localized, and the role of the copper atoms would be basically one of creating a potential having the required translational symmetry of the lattice. This approach is explained by Fig. 1, where the $p_{x'}$ oxygen orbitals are shown directed toward the neighboring oxygen atoms (rather than copper atoms, in the usual case); the orthogonal $p_{y'}$ orbitals are not shown in this figure.

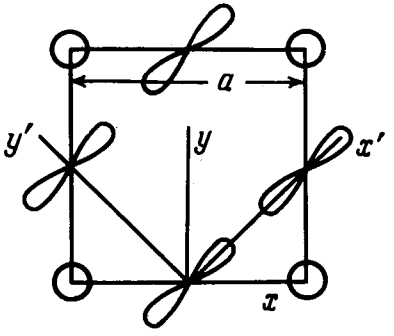

FIG. 1.

In the nearest-neighbor approximation we find two zones for a plane lattice:

$$\xi_{x'} = \xi_0 \cos\frac{k_x + k_y}{2} a - \xi_1 \cos\frac{k_y - k_x}{2} a, \quad \xi_{y'} = \xi_0 \cos\frac{k_y - k_x}{2} a - \xi_1 \cos\frac{k_x + k_y}{2} a, \quad (1)$$

where

$$\xi_0 = 2\langle p_{x'}(0,0)|V_0|p_{x'}(\tfrac{1}{2},\tfrac{1}{2})\rangle, \quad \xi_1 = -2\langle p_{x'}(0,0)|V_0|p_{x'}(-\tfrac{1}{2},\tfrac{1}{2})\rangle.$$

The coordinates of the oxygen atoms along the tetragonal axes x and y are given in parentheses, in units of the distance (a) between copper atoms.

The Brillouin zone for spectrum (1) is the Brillouin zone of an oxygen lattice with vectors $\mathbf{b}_0^{(1)} = 2\pi/a(1,1), \mathbf{b}_0^{(2)} = 2\pi/a(1,1)$. This zone is shown by the dashed lines in Fig. 2. The solid lines here are constant-energy surfaces corresponding to the equation $\xi_{x'} = \xi_{y'} = 0$. The hatching shows regions of negative energy in each zone.

The potential of the copper atoms, V_{Cu}, has a period greater than that of the oxygen lattice. It is this potential which determines the actual Brillouin zone. It is shown by the solid square with sides $\mathbf{b}_{\mathrm{Cu}}^{(1)} = 2\pi/a(1,0), \mathbf{b}_{\mathrm{Cu}}^{(2)} = 2\pi/a(0.1)$. Taking V_{Cu} into account, we can put spectrum (1) inside the actual Brillouin zone by means of the vectors $\mathbf{b}_{\mathrm{Cu}}$. We see from this figure that the entire zone turns out to be filled twice: There is a nesting, which is arranged by the conditions $\xi_\alpha(\mathbf{k} + \mathbf{b}_{\mathrm{Cu}}) = \xi_\alpha(\mathbf{k})$.

Up to this point we have examined the states of two p electrons (or two holes in a p shell). In all, there are four such electrons in the structural unit of the CuO_2 plane lattice. These electrons fill the Brillouin zone completely and twice. Two electrons in p_z atomic orbitals participate in an interaction of layers. For the electrons of the copper configuration, on the other hand, this model corresponds to a picture in which one of the $3d$ electrons, having escaped from a d shell, creates a localized angular momentum there and also participates in the formation of a filled $4s^2$ state.

A simple transfer of the spectrum into the actual Brillouin zone gives rise to a gapless state: The energy bands intersect along the solid curves in Fig. 2. In principle, this degeneracy can be lifted by the potential V_{Cu}, by the spin-orbit interaction in the

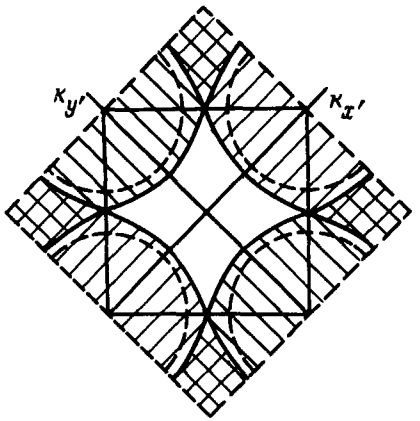

FIG. 2.

oxygen atom (λ), by hybridization with copper states, and by an antiferromagnetic order of the copper spins.

When V_{Cu} is taken into account, spectrum (1) becomes

$$\epsilon = \pm \frac{\xi_{x'} - \xi_{y'}}{2} \pm [(\frac{\xi_{x'} + \xi_{y'}}{2})^2 + u^2]^{1/2}, \tag{2}$$

where $u = \langle p_x,(0,0)|V_{\mathrm{Cu}}|p_y,(0,0)\rangle$ is the intracenter overlap integral. The interaction of nearest neighbors makes u dependent on the quasimomentum but does not alter the structure of the specrum. It can be seen from (2) that the intersection of the bands persists. The intersection now occurs on the curves which are defined by the equation $\xi_{x'}\xi_{y'} = -u^2$ and which are shown by the dashed line in Fig. 2. The spin-orbit counting λ is important near the same curves, and in their vicinity we find the following result for two intersecting bands:

$$\epsilon = \pm [\frac{(\xi_{x'}\xi_{y'} + u^2 - \lambda^2)^2 + 4u^2\lambda^2}{\xi_{x'}^2 + \xi_{y'}^2 + 2u^2 - 2\lambda^2}]^{1/2}.$$

Now the intersection has been eliminated: On the curves defined by the equation $\xi_{x'}\xi_{y'} + u^2 - \lambda^2 = 0$ a gap $\Delta = 4\lambda u|\xi_{x'}|/(\xi_{x'}^2 + u^2)$ has appeared. The value of $\xi_{x'}$ varies from the value of u at the intersection of these curves with the boundaries of the Brillouin zone to approximately u^2/ξ_0 at the intersection with the $k_{x'}, k_{y'}$ axes. Consequently, the gap takes on a value on the order of 2λ in a region with a linear dimension u near the boundaries of the Brillouin zone and has a value of $4\lambda u/\xi_0$ on nearly this entire curve. For estimates, here are some typical values of the parameters involved here:

$$\xi_0 = 3 \text{ eV}, \xi_1 = 1 \text{ eV}, u = 0.5 \text{ eV}, \lambda = 0.01 \text{ eV}.$$

Since the spin-orbit coupling is weak, hybridization must be taken into account. In conventional band calculations the hybridization with copper $d_{x^2-y^2}$ states is

taken into account, since it is assumed that specifically these states play an important role in shaping the entire band structure. In addition, we know that the s and d states in copper overlap in energy, and states with a larger angular momentum and the same energy should be localized to a greater extent. The hybridization with the s states should then be more substantial. This circumstance decouples the spin and transport electron subsystems and renders our model self-consistent. A calculation shows that the hybridization depends on the quasimomentum and that both the p-s hybridization and the p-d hybridization disappear on the $k_{x'}, k_{y'}$ axes. Introducing $\gamma = \langle p_{x'}(0,0)|V_0|s(\frac{1}{2},0)\rangle^2/(\epsilon_p - \epsilon_s)$, we can write the expansion

$$\epsilon = \pm (v_t^2 k_t^2 + v_l^2 k_l^2 + \Delta^2)^{1/2},$$

which is valid near each of the four extrema, which occur at the intersections of the degeneracy curves with the $k_{x'}, k_{y'}$ axes. Here k_t and k_l have been chosen to run perpendicular to and along the curves, $v_t \sim \xi_0 a, v_l \sim \gamma a$, and $\Delta \sim 4\lambda u/\xi_0$. Near an extremum the constant-energy curves are ellipses; in the region $u > |\epsilon| > \lambda, \gamma$ they are arcs, which run off in both directions from the dashed curve, to a distance $|\epsilon|/v_t$. Putting the origin in the Brillouin zone, we can transform these arcs into closed curves in such a manner that the region occupied by (for example) holes becomes a ring. Under the condition $|\epsilon| > u$ some additional pockets appear near the boundaries of the Brillouin zone. The shape of a constant-energy surface in this case is the same as that which is found in Ref. 2, but the filling of the states is radically different. Note also that the spectrum found here has the property of mirror symmetry: When the sign of ϵ is changed, the shape of the constant-energy surface does not change, but electrons appear where there were previously holes. For this reason, there should be no fundamental difference between electron and hole superconductors of this type.

We would like to say a few words about the kinetics in this model. At small values of the chemical potential, $|\epsilon_F| < T < \lambda u/\xi_0$, we have a semiconductor with a narrow band gap. Since a 2D spectrum arises in the region $\lambda u/\xi_0 \ll |\epsilon| \ll \gamma$, and a linear 1D spectrum in the region $\gamma \ll |\epsilon| \ll \xi_0$, the number of carriers increases initially quadratically with the temperature, and then linearly, in the nondegenerate case. This conclusion agrees with the behavior of the conductivity of several yttrium single crystals along the direction of the c axis (Ref. 4), if the carriers propagate by a tunneling mechanism. The linear behavior of the resistance in the a-b plane which has been observed is found over a wide temperature range in this model (in both the degenerate and nondegenerate cases) if the polarization mechanism for scattering by acoustic phonons is the governing mechanism.

The constant-energy curve shown in Fig. 2 is corrugated to an extent which depends on the ratio ξ_1/ξ_0 and thus differs from the familiar square in the model of p-d hybridization.[5] For this reason, a complete nesting does not occur in the case of an antiferromagnetic transition, when both of the new vectors of the Brillouin zone are shorter than $\mathbf{b}_0$ by a factor of two. The effect of the transition to an electron carrier spectrum turns out to be small, in proportion to the parameter T_N/ξ_1, and — the most important point — does not lead to singular terms in the total electron energy.

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