"Oxygen" picture of high-temperature superconductivity

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The picture of "holes on oxygen" is used to calculate the resistance, the transition temperature T_c, and the behavior of the "gap" near T_c.

Experiments are providing progressively more definite evidence that the current carriers in the high-temperature oxides are holes in a valence band associated with p states of oxygen (Ref. 1; see also Ref. 2). If this is the case, we find a physical picture in which the problems of magnetism and superconductivity are significantly separated. We are then essentially dealing with a heavily doped semiconductor. It contains a magnetic subsystem, which is formed by a hybridization of $Cu3d^9(x^2-y^2)$ and $Op(x,y)$ states and which is localized as a result of the Mott effect. The oxygen p states which are not involved in a hybridization form a valence band, in which the density of holes is determined by the stoichiometry. If the Fermi energy of the holes is large in comparison with the energy of the exchange interaction of holes with copper spins, the effect of this interaction on the spectrum and transport properties of the holes will be relatively weak. If necessary, it can be dealt with by perturbation theory. The Kondo effect presents no problems here, since there is a significant exchange (~ 0.1 eV) within the magnetic system. There is, of course, the separate question of the state of this system. A very attractive hypothesis has been advanced by Anderson.[3] According to that hypothesis, this state is a spin singlet with a fairly high carrier density.

Apparently the only interaction which could be responsible for the observed high values of T_c in this situation is an interaction of holes with phonons. A favorable circumstance is the presence of rich phonon spectra in such systems as La_2CuO_4 and $YBa_2Cu_3O_7$. Since the holes are genetically related to the oxygen, they should also interact effectively with high-frequency oxygen modes. As we will show below, this approach gives us the values of T_c which we need, even with an interaction constant $\lambda \sim 1$. We use the same model to calculate the temperature dependence of the resistivity, $\rho(T)$; it turns out to be linear over a wide range of T. Comparison with experimental data yields the further limitation $(m^*/m)\lambda \sim 1$. The effective hole mass m^* must therefore be close to the electron mass m. Unfortunately, we do not yet have any other even halfway reliable sources of information about the value of m^*. The band-theory calculations which have been carried out to date, beginning with Ref. 4, ignore Coulomb correlations and thus contain no data about the spectrum of oxygen holes. In this picture, the paramagnetic susceptibility should be assigned to the magnetic subsystem. Finally, the jump in the heat capacity at the transition point (data on which lead to anomalously large values of m^* in the ordinary interpretation) is a jump in the phonon heat capacity in the case of the high-temperature superconductors, as we will see below.

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Our calculation is based on several model assumptions, which we have kept as simple as possible where reliable information is lacking.

1. We eliminate from consideration a transport between CuO_2 layers; a single valence band (two-dimensional) corresponds to each layer; the density of holes in this band is x per square cell. For $YBa_2Cu_3O_7$ we would have $x = 0.5$.

2. The phonon spectrum (Refs. 5–7, for example) is simulated by three Einstein oscillators, whose frequencies ω_i form the ratios 1:3:5. In choosing an interaction we use the well-known relation

$$\lambda = 2\int_0^\infty d\omega \frac{\alpha^2(\omega)F(\omega)}{\omega},$$

and we assume that the constants α_i do not depend on the frequency, so the λ_i are inversely proportional to the frequencies ω_i.

We can now write an equation for T_c, putting it in a form with a symmetric kernel:

$$\chi_n = \frac{1}{[(2n+1)(1+\lambda(n))]^{1/2}} \sum_{n' \geqslant 0} \frac{1}{[(2n'+1)(1+\lambda(n'))]^{1/2}} D_+(n, n')\chi_{n'}. \quad (1)$$

where

$$\lambda(n) = \frac{1}{2n+1} \sum_{n' \geqslant 0} D_-(n, n'),$$

$$D_{+(-)}(n, n') = \sum_{i=1}^{3} \lambda_i u_i^2 \left[\frac{1}{u_i^2 + 4(n-n')^2} \underset{(-)}{+} \frac{1}{u_i^2 + 4(n+n'+1)^2}\right],$$

$$u_i = \hbar\omega_i / \pi T_c.$$

This expression is convenient for using a variational principle. With an accuracy sufficient for our purposes we find $T_c = 0.35\hbar\omega_1$ at $\lambda_1 = 1$ and $T_c = 0.5\hbar\omega_1$ at $\lambda_1 = 1.3$. The lower frequency ω_1 corresponds primarily to acoustic modes; the optimum estimate of it is $\hbar\omega_1 \approx 170$–$200$ K in the case of $YBa_2Cu_3O_7$. (It should be kept in mind that the maximum momentum transfer in the plane is $2p_F$.) The necessary T_c interval is thus provided by the vicinity of the value $\lambda = 1$. The introduction of a Coulomb pseudopotential in (1) has the same effect as a redistribution of the weight contribution toward lower frequencies.

Let us calculate the resistance for this model. Since large values of the momentum transfer are important at $T > T_c$, we can express $\rho(T)$ in terms of the damping of hole excitations:

$$\rho = \frac{m^*}{ne^2\tau}; \quad \frac{1}{\tau} = 2\pi\lambda_1\omega_1 f(t_1), \quad t_i = T/\hbar\omega_i \,, \tag{2}$$

$$f(t_1) = \left[\int_0^1 \frac{dx}{\sum_{i=1}^{3}\varphi(t_i, x)}\right]^{-1}; \quad \varphi(t,x) = \left[\sinh\frac{1}{t}\left(1 - x^2\tanh^2\frac{1}{2t}\right)\right]^{-1}.$$

The function $f(t_1)$ is shown in Fig. 1. The dashed line is the result found by reducing the contributions of the high frequencies ω_2 and ω_3 by a factor of 2/3. On the linear interval, line 1 is described by $f(t_1) = -0.3 + 1.6\ t_1$. The classical limit is actually reached at $t_1 > 5$ and corresponds to a slope of 1.53. If we use the results of Ref. 8, which rank among the best, we find $(m^*/m)\lambda_1 \approx 0.7$ for $YBa_2Cu_3O_7$. This value suggests that m^* should in fact be smaller than m. The limitation becomes slightly less stringent if the contribution of high frequencies of the phonon spectrum is reduced in the model. Nevertheless, we can say that a value $(m^*/m) = 5$ would definitely cast doubt on the entire picture. We should add that the mass we are talking about here is the mass which appears in the conductivity and which does not contain a Migdal normalization of the $1 + \lambda$ type.

The question of the jump in the heat capacity at the point of the transition becomes particularly important in connection with the discussion above. Specifically, if we use even the smallest of the published values,[9] $\Delta C_p = 2\ J/(\text{mole}\cdot\text{K})$, then by proceeding in accordance with the customary interpretation we would find a value for m^* which lies outside the range specified above. The data from more-recent measurements are even larger, by a factor of two or three. The situation changes qualitatively if we consider the ΔC_p component which stems from the change in the phonon free energy at the superconducting transition. At the usual values $T_c \lesssim 10$ K, the phonon heat capacity is itself comparable to or even less than the electron heat capacity, while in the case of $YBa_2Cu_3O_7$, for example, we have $C_p > 100\ J(\text{mole}\cdot\text{K})$ at $T = T_c$. This

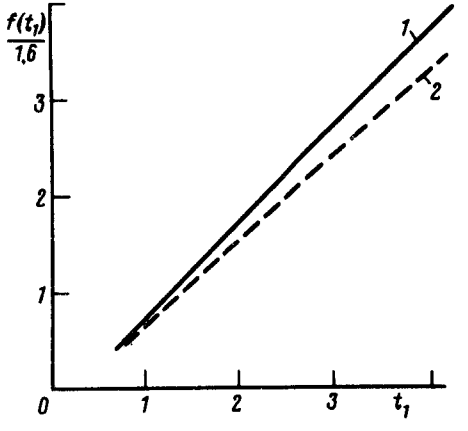

FIG. 1.

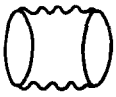

FIG. 2.

figure is more than two orders of magnitude greater than typical electron heat capacities. The component in which we are interested here is determined by the free-energy diagram in Fig. 2. (A general expression for the thermodynamic potential of the electron-phonon system is given in Ref. 10.) Each loop in this diagram contains the square of a "gap." In the equations for the eigenenergy parts of Σ_1 and Σ_2 (Ref. 10) this component corresponds to a correction $\sim\Sigma_2^2$ to the interaction kernel. An important point is that this component is negative:

$$\delta F=-\frac{1}{4}\sum_{i=1}^{3}\int\frac{d^3q}{(2\pi)^3}T\Sigma_\omega\left[D_i^{(0)}D_k^{(0)}\Pi_{ik}^2\right]_{q,\omega}. \tag{3}$$

It thus reduces the coefficient of ψ^4 in the expression for the Ginzburg-Landau free energy. Skipping over the details of the calculations, we write the final result, which gives the scale of the effect:

$$F=-a\psi^2+\frac{b}{2}\left(1-6\frac{T_c}{E_F}\ln\frac{E_F}{T_c}\right)\psi^4. \tag{4}$$

The coefficient, determined for $\lambda_1=1.3$ and for independent planes, should be increased further, by a factor of at least two, since the loops in the diagram in Fig. 2 may refer to different CuO_2 planes. With $E_F=0.6$ eV and $T_c=100$ K, there is a fivefold decrease in the coefficient of ψ^4. Although we do not give a great deal of credence to these numbers, we do reach the conclusion that this coefficient becomes an independent parameter under conditions of high-temperature superconductivity. In principle, it may turn out to be negative, in which case the superconducting transition would become a first-order transition. In this connection we might note that for dirty samples, in which the mean free path is determined by scattering by defects, the quantity $\ln(E_F\tau/\hbar)$ appears in (4), and the jump in the heat capacity decreases with increasing contamination.

Independently, there is an extremely marked variation in the structure of the equations below T_c: The superconducting order parameter must also be taken into account in the interaction kernel.

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