J. Phys. Chem. Solids Vol. 54, No. 10, pp. 1101–1107, 1993
Printed in Great Britain.

0022-3697/93 \$6.00 + 0.00
Pergamon Press Ltd

Color change and other unusual spectroscopic features predicted by the model of hole superconductivity

J. E. Hirsch
Department of Physics, University of California, San Diego, La Jolla, CA 92093-0319

ABSTRACT - The model of hole superconductivity postulates that the mobility of a hole carrier increases with the hole concentration in the system. From this single assumption follows the existence of superconductivity in the system in the regime of low hole concentration, and a number of unusual spectroscopic features: (1) Spectral weight in the frequency-dependent conductivity should be transfered from high to low frequencies in the normal state as the system is doped; (2) A similar spectral weight transfer in the frequency-dependent conductivity should occur for fixed carrier concentration as the temperature is lowered and the system becomes superconducting; (3) In the single-particle density of states, spectral weight transfer between positive and negative energies should occur when the system is cooled below T_c, leading to an asymmetry in tunneling and photoemission experiments: an enhanced spectral weight in photoemission and a corresponding decreased spectral weight in inverse photoemission, and a larger tunneling current in a negatively compared to a positively biased sample, should be seen; (4) In angle resolved photoemission the sharpest peaks in the normal and superconducting states should occur for different k-values, and in a range of k-values the peak should move *towards* the Fermi energy in the superconducting state while it is moving *away* from it in the normal state.

Keywords: sum-rule violation, hole superconductivity, color, asymmetry

INTRODUCTION

The model of hole superconductivity describes a dilute system of hole carriers whose hopping amplitude is a function of the local charge occupation. For a carrier of spin σ hopping between neighboring sites i and j the hopping amplitude is

$$t_{ij}^{\sigma} = t_h + \Delta t(n_{i,-\sigma} + n_{j,-\sigma}) \tag{1}$$

where $n_{i,-\sigma}$ is the number operator for holes of spin $(-\sigma)$ at site i. The parameters t_h and Δt have the same sign, and for application to high T_c oxides it is assumed that $\Delta t >> t_h$. Eq. (1) implies that the bandwidth increases as the hole concentration increases, as shown schematically in Fig. 1.

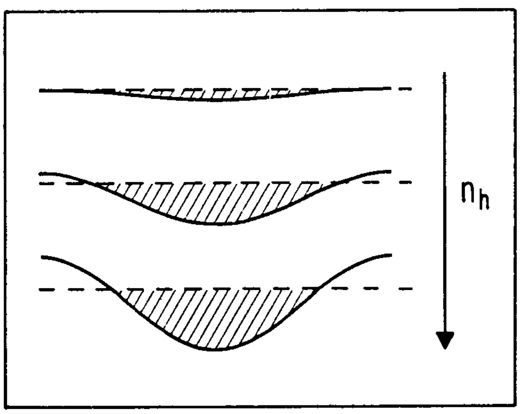

Fig. 1: The relevant electronic band for various hole contents (schematic). We expect this band to arise from overlap of O p_π orbitals in the planes.

Furthermore, Eq. (1) leads to the following consequences:

- Superconductivity occurs at low temperatures and low hole concentrations (Hirsch and Marsiglio, 1989; Micnas et al, 1989; Appel et al, 1993).
- The superconducting state is s-wave. The superconducting energy gap is constant over the Fermi surface, even if the Fermi surface is anisotropic (Marsiglio and Hirsch, 1989a).
- The energy gap varies strongly in directions perpendicular to the Fermi surface, with a linear energy dependence (Hirsch and Marsiglio, 1989).
- The gap ratio is larger than 3.53 for low hole concentrations and approaches 3.53 for higher hole concentrations.
- The superconducting coherence length increases monotonically with hole doping; a cross-over from strong to weak coupling regimes occurs as the hole concentration increases (Marsiglio and Hirsch, 1990a).
- A coherence peak in type II observables (electromagnetic absorption, NMR relaxation rate) is expected for large hole concentrations (Marsiglio and Hirsch, 1991).
- The transition temperature increases rapidly with pressure (Marsiglio and Hirsch, 1990b).
- The transition from the superconducting to normal state occurs through pair unbinding rather than Bose decondensation, even in the region of short coherence length (low hole doping) (Hirsch, 1989).
- The London penetration depth is shorter than expected from the normal state effective mass (Hirsch and Marsiglio, 1992a).
- Ferrell- Glover-Tinkham sum rule is violated, maximally so for low hole concentration (Hirsch, 1992a).
- Tunneling characteristics are asymmetric, the asymmetry has universal sign: larger current for a negatively biased sample (Marsiglio and Hirsch, 1989b).
- In direct photoemission, spectral weight increases in going from the normal to the superconducting state; in inverse photoemission it decreases (Marsiglio and Hirsch, 1989b; Hirsch, 1991a).
- The wave-vectors of the quasiparticle excitations of minimum energy in the superconducting state are not on the normal state Fermi surface but somewhat shifted towards higher hole band energies (Hirsch, 1991a).
- The critical temperature and the superconducting state are strongly affected by non-magnetic disorder (Marsiglio, 1992; Hirsch, 1992b; Wysokinski, 1992).
- The normal state effective mass decreases with increasing hole occupation (Hirsch and Marsiglio, 1992b).

Clear experimental evidence against any one of these predictions would establish the inapplicability of this model to describe the physics of high T_c oxide superconductors.

HAMILTONIAN

We consider the Hamiltonian

$$H = -\sum_{\substack{ij \\ \sigma}} t_{ij}^{\sigma}(c_{i\sigma}^{\dagger}c_{j\sigma} + h.c.) + U\sum_i n_{i\uparrow}n_{i\downarrow} + V\sum_{<ij>} n_i n_j \qquad (2)$$

with $c_{i\sigma}^{\dagger}$ a hole creation operator at site i. t_{ij}^{σ} , given by Eq.(1), describes the hopping of holes between $O^{=}$ anions in the $Cu - 0$ planes of high T_c materials, and U and V are on-site and nearest-neighbor Coulomb repulsions (positive). It is assumed that in the insulating state the band described by Eq.(2) (presumably the O $p\pi$ band in the plane) is full and that doped holes go into this band. Three-dimensional effects are described by adding a small hopping amplitude in the direction perpendicular to the planes, of the same form as Eq. (1) and with the same ratio of t_h and Δt parameters as in the plane (Marsiglio and Hirsch, 1990b).

Fig. 2 shows the behavior of critical temperature, coherence length and normal state effective mass versus hole concentration for a particular set of parameters, representative of a wide range of parameters. Other examples can be found in the references.

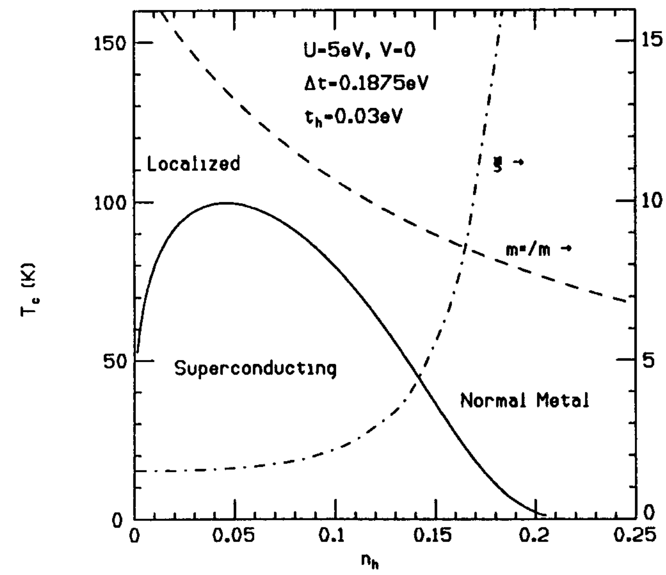

Fig. 2: T_c versus hole concentration n_h (corresponding to number of holes per planar oxygen) for a representative set of parameters. The behavior of the coherence length ξ and the ratio of normal state effective mass m^* to free electron mass m is also shown.

The BCS quasiparticle energy is given by

$$E_k = \sqrt{(\epsilon_k - \mu)^2 + \Delta_k^2} \tag{3a}$$

$$\Delta_k = \Delta_m(-\frac{\epsilon_k}{D/2} + c) \equiv \Delta(\epsilon_k) \tag{3b}$$

where D is the bandwidth, μ the chemical potential and the parameters Δ_m and c are determined from solution of the BCS equations. The gap function Eq. (3b) vanishes for $\epsilon_k/(D/2) = c$. However, since solution of the equations leads to $c > \mu/(D/2)$, the quasi-particle energy Eq.(3a) never vanishes. The minimum quasi-particle excitation energy is

$$\Delta_0 = \frac{\Delta(\mu)}{a} \tag{4a}$$

$$a = (1 + (\frac{\Delta_m}{D/2}))^{1/2}, \tag{4b}$$

and Eq.(3a) can be rewritten as

$$E_k = \sqrt{a^2(\epsilon_k - \mu - \nu)^2 + \Delta_0^2} \tag{5}$$

with

$$\nu = \frac{1}{a}\frac{\Delta_m}{D/2}\Delta_0. \tag{6}$$

Fig. 3 shows schematically Δ_k and E_k versus hole band energy.

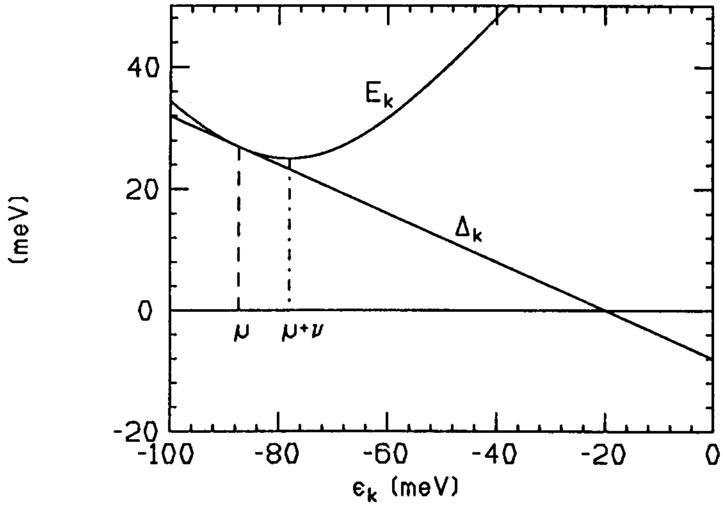

Fig. 3: Gap function Δ_k and quasiparticle energy E_k versus hole band energy ϵ_k. Parameters are: $D = 200meV$, gap slope $\Delta_m/(D/2) = 0.4$, $c = -0.2$, $\Delta_0 = 25meV$. Only the lower half of the hole band (upper half of the electron band) is shown. Note that the minimum in the quasiparticle energy is shifted from the chemical potential.

SINGLE PARTICLE SPECTRAL FUNCTION

The quasi-particle spectral density is given by the usual form

$$I_0(k,\omega) = u_k^2\delta(\omega + E_k) + v_k^2\delta(\omega - E_k) \tag{7}$$

with

$$u_k^2 = \frac{1}{2}(1 + \frac{\epsilon_k - \mu}{E_k}) \tag{8a}$$

$$v_k^2 = \frac{1}{2}(1 - \frac{\epsilon_k - \mu}{E_k}). \tag{8b}$$

A photoemission experiment measures $I_0(k,\omega)f(\omega)$, with $f(\omega)$ the Fermi function, while an inverse photoemission experiment measures $I_0(k,\omega)f(-\omega)$. ω is the initial state energy measured with respect to the chemical potential.

In a photoemission experiment the first term is Eq.(7) dominates at low temperatures. The form of the quasiparticle energy Eq.(5) implies that the peak in the photoemission spectrum closest to the Fermi energy occurs for

$$\epsilon_k = \mu + \nu \tag{9}$$

for which

$$u_k^2 = \frac{1}{2}(1 + \frac{\nu}{\Delta_0}). \tag{10}$$

The amplitude Eq (10) is larger than 1/2, the value expected in a conventional superconductor, implying a larger signal of the transition to the superconducting state in a photoemission experiment than in the usual case. In contrast, in an inverse photoemission experiment the second term in Eq. (7) dominates and since it is smaller than 1/2 at the minimum excitation energy

$$v_k^2 = \frac{1}{2}(1 - \frac{\nu}{\Delta_0}) \tag{11}$$

a weaker signal of the transition is expected. Typical parameters in the model yield values of ν/Δ_0 of 0.2 to 0.4.

In addition the surface in momentum space defined by Eq.(9) is shifted from the normal state Fermi surface $\epsilon_k = \mu$ by an amount

$$\Delta k = \frac{\nu}{\hbar v_F(k)} \tag{12}$$

with $v_F(k)$ the Fermi velocity at point k of the normal state Fermi surface. This new Fermi surface encloses more hole states (less electron states) than the original one.

The spectral density Eq. (7) integrated over momenta yields (Marsiglio and Hirsch, 1989b)

$$I_0(\omega) = \rho \left[\frac{-\omega + \nu}{a\sqrt{\omega^2 - \Delta_0^2}} \theta(-\omega) + \frac{-\omega - \nu}{a\sqrt{\omega^2 - \Delta_0^2}} \theta(\omega) \right] \tag{13}$$

for a constant normal state density of states ρ. Eq.(13) implies that net gain (loss) in spectral weight will occur in direct (inverse) photoemission in going from the normal to the superconducting state. (The same asymmetry is expected in $N - I - S$ tunneling experiments.) The added spectral weight in photoemission is transfered from low energy states of positive energy rather than from high energy states as predicted by other theories (Anderson, 1990).

Quantitative estimates of the magnitude of these effects in direct and inverse photoemission are given elsewhere (Hirsch, 1991a). It should be kept in mind however that these results apply to the states of the narrow oxygen band that drives superconductivity within this model; spectral features of states originating in other bands could be rather different.

OPTICAL SPECTROSCOPY

The conductivity sum rule in a tight binding model yields (Maldague, 1977)

$$\int_0^{\omega_m} d\omega\, \sigma_1^{\delta\delta}(\omega) = \frac{\pi e^2 a_\delta^2}{2\hbar^2} < -T_\delta > \tag{14}$$

with $\sigma_1^{\delta\delta}(\omega)$ the frequency-dependent conductivity in direction δ, a_δ the lattice spacing in direction δ, ω_m a band energy cutoff and $< T_\delta >$ the expectation value of the kinetic energy in direction δ:

$$T_\delta = -\sum_{i,\sigma} t^\sigma_{i,i+\delta}(c^\dagger_{i\sigma} c_{i+\delta,\sigma} + h.c.). \tag{15}$$

When carriers pair the expectation value of Eq.(15) decreases due to the dependence of t^σ_{ij} on the local hole occupation Eq(1). Hence the intra-band spectral weight Eq.(14) increases. Similarly, upon doping in the normal state the average value of t^σ_{ij} increases and a transfer of spectral weight into intra-band processes is predicted by the Hamiltonian Eq.(2). Such transfer of spectral weight in the normal state with doping has apparently been observed (Uchida et al, 1991; Cooper et al, 1992). Its counterpart expected to occur as the system enters the superconducting state has not been clearly established experimentally to our knowledge.

This added low energy spectral weight arises from a decrease in the weight of optical transitions to high energy states not described by the low-energy Hamiltonian Eq. (2). To understand the origin of this spectral weight transfer it is necessary to return to the more fundamental Hamiltonian from which the effective Hamiltonian Eq.(2) and in particular the term Δt was originally derived (Hirsch and Tang, 1989; Hirsch and Marsiglio, 1990). It is found that this peculiar property of intimate coupling of high energy physics involving optical processes in the infrared and visible range, and the low energy physics associated with the pairing energy gained upon entering the superconductivity state, is a general feature of a certain class of non-linear polaronic models (Hirsch, 1992c). Such models can arise both from a description of purely electronic processes (Hirsch, 1991b) as well as from electron-phonon interactions (Pincus, 1972; Hirsch, 1993a). The physics described by these models is that the "dressing" of quasi-particles is a function of the local carrier concentration. When the hole concentration increases locally, either by pairing or by hole doping, carriers partially "undress".

Experimentally, this physics should be apparent from observation of a shorter London penetration depth than expected from the normal state effective mass, particularly for low hole concentration (Hirsch and Marsiglio, 1992b) and from observation of transfer of spectral weight from high frequencies (visible and infrared) to lower (intra-band or zero) frequencies upon doping and upon entering into the superconducting state (Hirsch, 1992a; 1992c). Quantitative details are given in the references.

As for comparison with other models: it appears that in the ordinary Hubbard model an increase in conductivity spectral weight at low frequencies is also expected upon doping, but not upon entering the superconducting state (Scalapino, unp.). In the interlayer pair transfer model (Anderson, 1991) a lowering of the kinetic energy in the c-direction is expected upon entering the superconducting state, but not in other directions. Thus, experiments should be able to distinguish between those models and the model discussed here. To our knowledge, in those models no explanation for the origin of the extra spectral weight appearing at low energies has been proposed.

DISCUSSION

The predictions of the model of hole superconductivity are sufficiently definite that the model can be clearly ruled out or strongly supported by future experiments. For example, recent experimental claims of large in-plane anisotropy in the gap function (Shen et al, 1993) and of intrinsic linear behavior in the London penetration depth versus temperature (Hardy et al, 1993) would rule the model out, if confirmed. On the other hand, observation of the predicted behavior in optical and photoemission experiments discussed in the previous sections would strongly support the model.

We have not addressed here high energy features in photoemission and inverse photoemission experiments that would arise from "non-diagonal" transitions in the underlying polaronic model that gives rise to the effective Hamiltonian Eq.(2). Some of these effects have recently been discussed (Alexandrov and Ranninger, 1992).

Effects associated with the $Cu\ d_{x^2-y^2} - Op_\sigma$ orbitals can be described in the context discussed here by considering a two-band model of the type introduced by Suhl et al (Suhl et al, 1959; Hirsch and Marsiglio, 1991; Hong and Hirsch, 1992). This extended model may explain various observed properties of high T_c materials without altering the essential physics described in the previous sections. Some of the observed anomalous normal state properties may be explained within the model discussed here by allowing for a variation of the number of charge carriers in the planes with temperature (Moshchalkov, 1990; Hirsch and Marsiglio, 1992a).

We have mentioned some remarkable similarities of the model discussed here and the RVB model (Anderson, 1991) as well as some important differences. Another crucial difference between both models concerns the expected behavior of T_c under uniaxial pressure, under conditions where the number of carriers in the plane is kept constant (or the effect of change in the number of carriers in the plane is substracted out (Neumeier and Zimmermann, 1993)). Once this behavior is clearly established experimentally it will rule out at least one of the two models. Anderson's model is incompatible with observation of negligible pressure dependence of T_c in directions perpendicular to the planes and large positive pressure dependence of T_c in directions parallel to the planes (Anderson, 1992), the behavior predicted by our model (Marsiglio and Hirsch, 1990b); our model is incompatible with observation of large positive pressure dependence of T_c in direction perpendicular to the planes and negative pressure dependence of T_c in directions parallel to the planes, the behavior predicted by Anderson's model. Observation of neither behavior would rule out both models.

In closing we mention that the assumption underlying the behavior of hopping amplitudes in the model of hole superconductivity, Eq.(1), is supported by first-principles calculations of electronic hopping amplitudes in small molecules (Hirsch, 1990, 1993b).

ACKNOWLEDGEMENTS

The author is grateful to F. Marsiglio for collaboration in this work, and to the National Science Foundation and the University of California, San Diego for partial financial support.

REFERENCES:

Alexandrov, A.S. and Ranninger, J. (1992). Physica C **198**, 360.
Anderson, P.W. (1990). Phys. Rev. **B42**, 2624.
Anderson, P.W. (1991). Physica C **185-189**, 11.
Anderson, P.W. (1992). Science **258**, 672.
Appel, J., Grodzicki, M. and Paulsen, F. (1993). Phys. Rev. **B47**, 2812.
Cooper, S.L. et al (1992). Phys. Rev. **B45**, 2549.
Hardy, W.N. et al (1993). Preprint.
Hirsch, J.E. (1989). Physica C **161**, 185.
Hirsch, J.E. (1990). Chem. Phys. Lett. **171**, 161.
Hirsch, J.E. (1991a). Physica C **182**, 277.
Hirsch, J.E. (1991b). Phys. Rev. **B43**, 11400.
Hirsch, J.E. (1992a). Physica C **199** , 305.
Hirsch, J.E. (1992b). Physica C **194** , 119.
Hirsch, J.E. (1992c). Physica C **201**, 347.
Hirsch, J.E. (1993a). Phys. Rev. **B47**, 5351.
Hirsch, J.E. (1993b). Preprint.
Hirsch, J.E. and Marsiglio, F. (1989). Phys. Rev. **B39**, 11515.
Hirsch, J.E. and Marsiglio, F. (1990). Phys. Rev. **B41**, 2049.
Hirsch, J.E. and Marsiglio, F. (1991). Phys. Rev. **B43**, 424.
Hirsch, J.E. and Marsiglio, F. (1992a). Physica C **195**, 355.
Hirsch, J.E. and Marsiglio, F. (1992b). Phys. Rev. **B45**, 4807.
Hirsch, J.E. and Tang, S. (1989). Phys. Rev. **B40**, 2179.
Hong, X.Q. and Hirsch, J.E. (1992). Phys. Rev. **B45**, 12556.
Maldague, P. (1977). Phys. Rev. **B16**, 2437.
Marsiglio, F. (1992). Phys. Rev. **B45** , 956.
Marsiglio, F. and Hirsch, J.E. (1989a). Physica C **163-164**, 1451.
Marsiglio, F. and Hirsch, J.E. (1989b). Physica C **159**, 157.
Marsiglio, F. and Hirsch, J.E. (1990a). Physica C **165**, 71.
Marsiglio, F. and Hirsch, J.E. (1990b). Phys. Rev. **B41**, 6435.
Marsiglio, F. and Hirsch, J.E. (1991). Phys. Rev. **B44**, 11960.
Micnas, R., Ranninger, J. and Robaszkiewicz, S. (1989). Phys. Rev. **B39**, 11653.
Moshchalkov, V.V. (1990). Sol. St. Comm. **73**, 777.
Neumeier, J.J. and Zimmermann, H.A. (1993). Preprint.
Pincus, P. (1972). Sol. St. Comm. **11**, 51.
Scalapino, D.J. private comm.
Shen, Z.X. et al (1993). Phys. Rev. Lett. **70**, 1553.
Suhl, H., Matthias, B.T. and Walker, L.R. (1959). Phys. Rev. Lett. **63**, 552 .
Uchida,S. et al, (1991). Phys. Rev. **B43**, 7942.
Wysokinski, K.I. (1992). Physica C **198** , 87.