Interim report on the charge-transfer resonance model for the Cu–O superconductors

by C. M. Varma

The two-band model including intra-atomic repulsion on Cu and near-neighbor Cu–O repulsion for the high-temperature superconductors is supported by a variety of experiments and theoretical calculations as the minimum necessary. The specific mechanism for high T_c through charge-transfer resonances was proposed because the known alternative mechanisms—phonons and magnetic excitations—were believed unlikely. The case for charge-transfer-resonance-induced high T_c has, however, not yet been proven. Equally important, the various anomalies in the metallic state are not yet understood. However, calculations on the model do show a charge-transfer-gap insulating state which is antiferromagnetic at and near 1/2 filling, a metallic state for intermediate filling with effective particle–particle attraction, and a charge-transfer instability beyond a certain filling.

Physical basis for the model

The physical basis underlying the model [1, 2] is constituted by the following ideas.

1. The metallic phase is similar to a Fermi liquid. By this is meant that the phase continued to $T = 0$ has a Fermi surface, and that it contains a number of quasiparticles consistent with Luttinger's theorem. The existence of the Fermi surface, broadened by not much more than the temperature, should not now be considered in doubt, following the remarkable photoemission experiments [3] with 20-meV resolution. Positron annihilation experiments [4] for the momentum distribution have been reported to be consistent with Luttinger's theorem—indeed more than that: with the bandstructure. The resolution on these experiments is, however, not completely conclusive. If this point is confirmed, it should rule out, as well as resonant valence bonds (RVB), the models which presume the existence of localized moments on Cu with holes moving on the oxygen in the metallic phase.

In opposition to the hypothesis of a Fermi-liquid phase for these materials are the normal-state resistivity, the non-Korringa nuclear relaxation rate, and various other transport properties which are unlike those expected in a degenerate Fermi liquid. It appears that there is a high density of excitations with energy low enough that temperature sets the scale for inelastic processes rather than the Fermi energy.

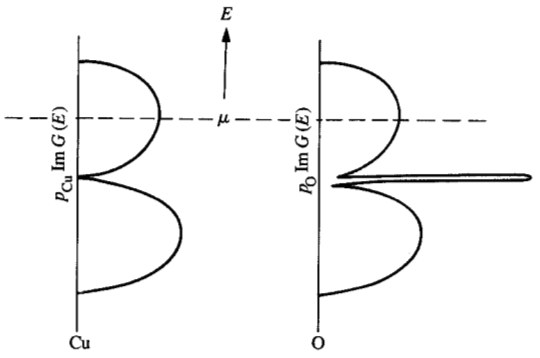

Figure 1

Schematic one-particle partial spectral weight on Cu atoms and on O atoms from the band structure part of model Hamiltonian, Equation (1).

This aspect of the phenomena must be understood before one can claim to have a theory for the Cu–O superconductors.

2. Strong correlations exist on the Cu atoms. Evidence for this is, of course, the antiferromagnetism at 1/2 filling [5]. Superconductivity in the metallic phase was, however, assumed not related to the possible magnetic correlations due to the electron–electron repulsion on Cu. Eliashberg theory using such correlations gives too low an upper limit to T_c [6]. Monte Carlo calculations on models incorporating such correlations alone (the one-band Hubbard model) give no sign of high-temperature superconductivity. In any case, recent neutron-scattering measurements [7] give magnetic correlation length in the metallic state of only about two lattice constants.

3. The Hubbard model is inadequate for discussing the low-energy physics of Cu–O compounds. This point was made on the basis of the systematics of transition-metal compounds—as one moves to the right of the periodic table, the ionization levels of Cu are close to those of oxygen [1, 2]. A single-band model is then suspect. Band structure calculations [8], which must get the electrostatic energies nearly right, give the Cu level $\epsilon_d \approx \epsilon_p$, the oxygen level at the self-consistent charge distribution. In such a situation the interatomic electron–electron repulsion (parameterized in the model by the nearest-neighbor Cu–O repulsion V), which is responsible for the stability of the ionic backbone to begin with, has an important *dynamic* role to play. The following model Hamiltonian was proposed:

$$H = \epsilon \sum_i (c^\dagger_{di} c_{di} - c^\dagger_{xi} c_{xi} - c^\dagger_{yi} c_{yi}) + \sum_{\langle ij \rangle} (t_{ij} c^\dagger_{di} c_{xj} + \text{h.c.} + x \rightarrow y) + \frac{1}{2} U \sum_i \delta n_{di} \delta n_{di} + V \sum_{\langle ij \rangle} \delta n_{di} (\delta n_{xj} + \delta n_{yj}). \quad (1)$$

Here $\epsilon = 1/2(\epsilon_d - \epsilon_p)$, and $\langle ij \rangle$ denotes nearest-neighbor summation. It may be necessary to supplement the model with a direct O–O hopping term. The conduction electron density in these materials is so low that the screening length is larger than the Cu–O separation. In this situation $V \approx e^2/(\epsilon_\alpha a)$, where ϵ_α is the high-frequency dielectric constant which at an energy of about 2 eV is $\approx$4, and a is the Cu–O distance $\approx$1.9 Å. V is then about 2 eV.

This two-band model reduces to the Hubbard model if $E_x \gg U$, where

$$U = E(Cu^{3+}) + E(Cu^{+}) - 2E(Cu^{2+})$$

and

$$E_x = E(Cu^{2+} + O^{2-}) - E(Cu^{+}) - E(O^{-}).$$

If the charge-transfer energy $E_x < U$, the material is an insulator at 1/2 filling for $E_x > 2t$, with a gap determined by E_x. Note that E_x is not equal to $|\epsilon_d - \epsilon_p|$ due to the influence of V [9]. $\epsilon_d - \epsilon_p$ is measured in one-particle spectroscopy like photoemission, and E_x in particle-hole spectroscopy. The model gives an AFM ground state near 1/2 filling for $U \gg E_x$. A variety of spectroscopic techniques directly support the two-band model. Recent careful photoemission measurements indicate a roughly equal admixture of Cu and O states near the Fermi level [10]. Optical experiments show that the oscillator strength in the metallic phase integrated to about 1 eV is about a factor of 2 larger than that expected for the total number of electrons in the conduction band [11]. Interband transitions below this energy range are then needed. Since band structure does not give interband transitions at such low energies in adequate measure, excitonic effects due to V appear to be called for. In the insulating phase, Raman scattering reveals, besides two-magnon scattering, a strong broad transition of a symmetry consistent with the breathing mode of Cu-to-oxygen charge-transfer resonance.

One-particle excitation spectra

The one-particle excitation spectrum projected on Cu and oxygen atoms is given by the spectral function of the one-

particle Green's function,

$$S_\alpha(\omega) = \frac{1}{\pi} \sum_k \langle \psi_k | \phi_\alpha \rangle^2 \delta(\omega - \epsilon_k), \qquad \alpha = \text{Cu, O.}$$

$S_\alpha(\omega)$ on the basis of one-electron theory for Equation (1) is schematically shown in **Figure 1**. We contrast it with the corrections expected with many-body theory. The spectral function below the chemical potential μ, i.e., the one-hole spectrum, is measured in the photoemission experiments, while its value above, the one-electron spectrum, is measured in the inverse photoemission experiments. Note that in the simplest scheme $\epsilon_d = \epsilon_p$, $t_2 = 0$, and the average valences are $Cu^{1.5+}$ and $O^{1.75-}$. With finite O–O hopping and/or ϵ_d above ϵ_p, one gets closer to Cu^{2+} and O^{2-}.

The *expected* actual partial spectral weight in the insulating state is shown in **Figure 2**. We consider the case $U_p \ll U_d$. The correlation energy due to many-body effects pushes the one-hole spectral weight on Cu down in energy compared to the mean-field result of Figure 1. The one-hole spectral weight is the relative strength for creating the excitations $Cu^{2+} \rightarrow Cu^{3+}$ at different energies. Meanwhile, the one-electron spectral weight, that for creating the excitations $Cu^{2+} \rightarrow Cu^{1+}$, moves up in energy, so that at the chemical potential the one-particle Green's function has zero spectral weight. There is then a magnetic moment of spin 1/2 on the Cu atoms. These spectral weights are often called the lower and upper Hubbard bands. Actually, there is hardly any band-like feature to them; they are mostly incoherent. What little (coherent) quasiparticle part exists [12] is due to the quantum nature of spins. The precise bandwidth of both the one-hole and the one-electron spectral weights depends upon the ordered magnetic structure but is of the order of (a little smaller than) the one-electron bandwidth. The difference of the centroid of the one-electron and one-hole spectral weights on Cu is the parameter U_d. The relevant partial oxygen spectral weight is all of the hole kind, giving O^{2-}. The Coulomb parameter V has also an important many-body role (i.e., beyond fixing $\epsilon_p - \epsilon_d$) to play in fixing the relative distribution. It pushes the Cu-hole spectral weight down with respect to the oxygen-hole spectral weight.

The picture in Figure 2 is consistent with experimental results on photoemission and inverse photoemission which show a gap of about 2 eV. In optical experiments, a particle-hole pair is created so that the attractive interaction between the particle and hole renormalizes the gap. The dipole matrix element exists for the excitation $Cu^{2+}O^{2-} \rightarrow Cu^{+}O^{-}$, so that the attractive interaction involves the parameter V.

Given the structure of the Cu–O planes, the largest effect of the parameter V in lowering the energy of the charge-transfer excitations is in a symmetric charge-transfer mode of Cu and oxygen. This is dipole-disallowed but Raman-active. We would therefore expect a Raman intensity at energies lower than those observed optically.

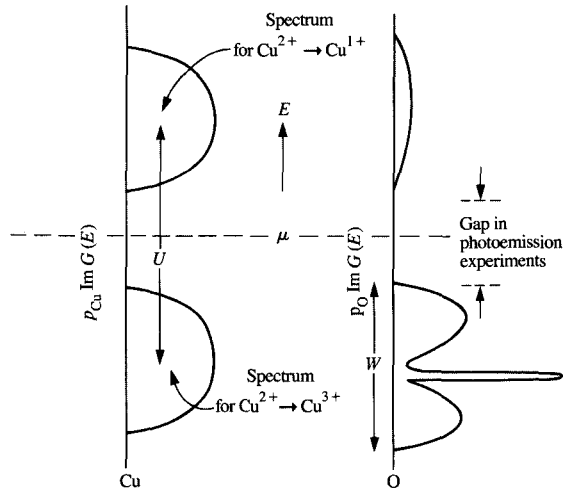

Figure 2

Schematic one-particle partial spectral weight on Cu atoms and on O atoms expected in the insulating state (at 1/2 filling) on the basis of the model Hamiltonian, Equation (1).

Note that if the large width of the hole and electron spectral weights were not taken into account, one would come to a rather different estimate of the parameters $\epsilon_d - \epsilon_p$, U_d, etc. in order to reconcile the model with the experimental results.

The insulating phase is an antiferromagnet. The motion of a hole or electron is then accompanied by excitations of spin-waves. This has been discussed in [12].

Imagine that the material is doped with holes so that the material above a critical concentration is a metal. The passage from the insulator to the metallic phase is nonanalytic, but certain features of the spectral weight, especially those at very high positive or negative energy, will remain similar to those of the insulating case, Figure 2. The conjectured spectral weight for the metallic state is shown in **Figure 3**.

Note that if the metallic state is a Fermi liquid near $T = 0$, the state can be *analytically* obtained from perturbation theory, starting from band structure calculations. In particular, Luttinger's theorem that the volume inside the Fermi surface does not alter with increasing interactions must be obeyed. This question is closely connected to the absence or presence of localized magnetic moments on Cu in the metallic phase. If the magnetic moments are present (as they are in rare-earth metals), the volume in the Fermi surface is given by the number of holes. If the magnetic

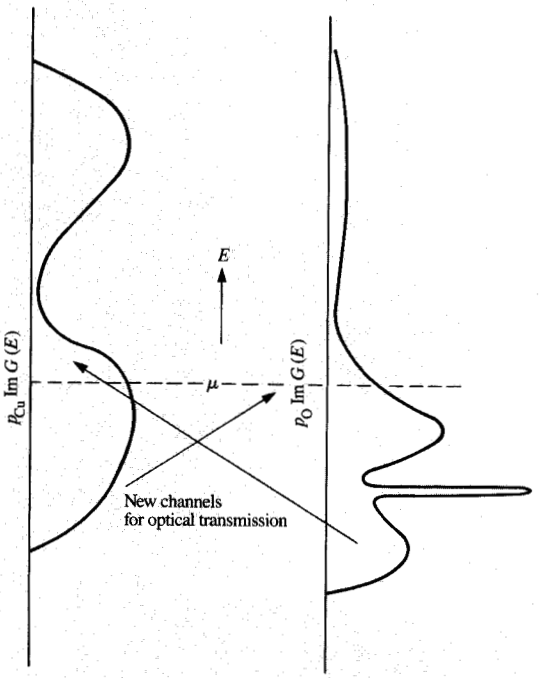

Figure 3

Schematic one-particle partial spectral weight on Cu atoms and on O atoms expected in the metallic phase on the basis of the model Hamiltonian, Equation (1).

moments *are* present, they must be magnetically ordered (or RVB). Elementary considerations indicate that the ordering temperature in the metallic phase cannot be much smaller than that in the insulating phase. Since no magnetic ordering is experimentally found in the metallic phase, models [13] which assume the existence of local moments on Cu have dubious validity.

Of the known or conjectured states, only a Fermi-liquid model, as for the heavy fermions, or RVB [14] may then be considered. Here we consider only the Fermi-liquid model.

In Figure 3, the one-electron and one-hole spectral weights join smoothly at the chemical potential, as required for a metal. The large correlation on Cu implies that the bulk of the one-electron and the one-hole spectral weights on Cu are still separated by an energy of order U. The spectral weight need not anywhere be zero, however, since dressing of a single particle with particle–hole pairs of arbitrarily low energy is possible.

Because of the continuous distribution of spectral weights, one-particle measurements will yield broader results than in the insulator. Two-particle excitations will also be much broader, since they now overlap the single-particle–hole continuum. Note also, as shown in Figure 3, that new channels for interband excitation, not present in the insulator, open up in the metallic phase. The general features of the spectral distribution can be obtained even in RPA, starting from the band structure. This is because at high T_c the self-energy at Cu in RPA behaves as

$$\sum(\omega) \sim U^2/\omega \qquad \omega \gg U.$$

The detailed features involving the physics of the disappearance of the static magnetic moments constitute a more subtle feature which doubtless involves the same physics as heavy fermions and mixed-valence materials. But the hybridization of the Cu d states with oxygen p states relative to the Cu–O energy separation is here a large parameter. The effective Kondo temperature is then of the same order as the hybridization energy. This must be considerably larger than the magnetic interaction energies to obtain Fermi-liquid behavior.

The results expected for photoemission and optical experiments are self-evident from Figure 3. One should note that again the lowest-energy charge-transfer mode is only Raman-active. It will in general interfere with the Drude absorption and change the latter's lineshape. Therefore, in optical experiments we expect both extra absorption due to interband charge-transfer excitations as modified by V, and an alteration of the Drude lineshape. The charge-transfer excitations in general transfer some of their spectral strength to phonons. The theory of this phenomenon has been worked out, and evidence of large spectral strength in phonons has been presented.

Microscopic calculations

Several calculations have been reported on the model Hamiltonian (1). Exact diagonalizations on small clusters reveal [15] that for large U, pairs of holes bind on oxygen atoms for large enough V. In two dimensions this is a necessary but not sufficient condition for superconductivity. The calculated binding of holes more likely signals a phase separation into regions of high and low hole density. Variational calculations based on extensions of Gutzwiller wavefunctions reveal this quite clearly [16]. Perturbation calculations in t/U and t/V are consistent with these results [17]. The variational calculations show that for a fixed V, the instability occurs as the hole concentration is increased.

A completely different method of calculations by Littlewood [18], based on weak coupling expansion in U/t and V/t, examines the one- and two-particle excitation spectra in the metallic phase. These results should be qualitatively correct if the metallic phase is a Fermi liquid. Besides the spin-fluctuations, the calculation finds various charge-transfer resonances, the strongest of which is of the Cu–O breathing-mode variety. This is observable by Raman

scattering. For fixed U/t, V/t, the Fermi-liquid phase is found to be unstable to a magnetically ordered phase at low doping through the softness of the spin-fluctuation modes. With increasing doping, the charge-transfer mode softens, leading to the instability of the assumed Fermi-liquid phase. This result is consistent with the instability in the other calculations mentioned above.

All Cu–O superconducting materials are antiferromagnetic at 1/2 filling, metallic at intermediate filling, and unstable beyond a certain doping [19]. In $YBa_2Cu_3O_x$, it is impossible to dope beyond $x \approx 7$. In $La_{2-x}Sr_xCuO_4$, increasing x beyond about 0.35 is not ordinarily possible; oxygen begins to leak out. This instability is consistent with the instability observed in the calculations. We believe that this instability is the key to high-temperature superconductivity. The highest T_c in the well-understood case of phonon-induced superconductivity occurs near the boundary of the lattice instabilities promoted by the same phonon modes which promote superconductivity. At present, we are examining the symmetry and the rough magnitude of T_c obtainable by the charge-transfer resonance modes.

It is by no means obvious that a purely repulsive model promotes superconductivity through the resonances we have in mind. We have argued [1, 2] that this can indeed happen only with strong local field corrections and with special features of the electronic structure. The discovery of high T_c ($\approx$30 K) in $Ba_{1-x}K_xBiO_3$ [20], which is outside the range for electron–phonon interactions, and where there is no question of magnetic correlations, supports the idea of a polarization or charge-transfer resonance-induced superconductivity. In these materials also, the highest T_c is at the boundary of an instability—one to a charge-disproportionated state [21].

Summary

The two-band model proposed for the Cu–O superconductors is supported by a variety of experiments. These materials at 1/2 filling are indeed charge-transfer insulators. The feasibility of the idea of high T_c through charge-transfer resonances is not proven, but well-defined calculations should soon have something to say about it. Calculations do show a large pairing attraction for substantial hole doping as a function of the Cu–O repulsion. They predict a dielectric instability which is consistent with observations. The important question is whether high T_c can arise in the metallic phase not too far from this instability.

A good theory should account for the various anomalies in the normal state—the resistivity and the nuclear relaxation rate, for example. In common with everyone else, we have not been able to come up with anything new on this aspect.

The idea of high T_c through charge-transfer resonances was proposed because we felt the alternative known mechanisms, phonon-induced or magnetically-induced, are understood enough to state convincingly that they could not lead to high T_c. Nothing experimental or theoretical has happened to change our mind. We cannot claim yet to have proven our point about charge-transfer resonances either.

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