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# Superconducting cuprates—phenomena and ideas five years later

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**Abstract**

The normal metallic state of the superconducting cuprates appears to be qualitatively different from known metals. Some of these unusual properties are described after a brief introduction. A number of ideas proposed to explain the normal state are mentioned briefly and a new approach is outlined.

**Key words:** Superconductivity, cuprates.

## 1. Introduction

The world became aware in 1986 of an oxide which becomes superconducting at about 35K[1]. The oxide was identified later as $La_{2-x}Sr_xCuO_4$ with $x \simeq 0{\cdot}15$. Very soon, in late 1986, a new compound, $YBa_2Cu_3O_7$ was discovered[2], with a $T_c$ of about 90K. With this discovery, superconductivity came out of the very cold and entered the liquid nitrogen age. (Liquid nitrogen is an industrial product, about as expensive as milk). These events were accompanied by unprecedented hype, hoopla and euphoria, followed a little later by an equally unjustified period of gloom. Now, after a lot of hard work, backed by modern science (and technology, art and magic) of materials preparation as well as characterization, a few applications are at hand and many others are real prospects[3].

Nearly twentyfive thousand papers have been published on this subject. Consequently, a very large amount of information on these complex and unusual systems is available, enough to constrain or overconstrain possible theories. In spite of all this, there is no agreement on a theory. Part of the reason is that in this field, standards are very high, being set by the Landau theory of normal metals, and the Bardeen, Cooper Schrieffer–Ginzburg Landau theory of superconductivity. I now describe briefly some properties of cuprate superconductors and then summarize some of the models developed for their normal as well as superconducting state. Some essential ingredients of a basic theory are then pointed out.

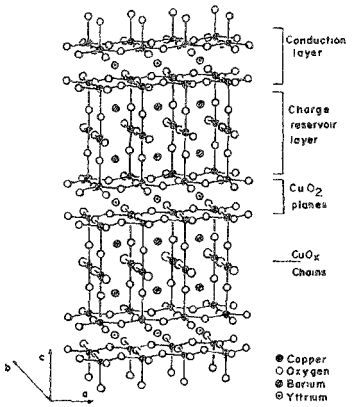


FIG. 1 Structure of $YBa_2Cu_3O_7$.

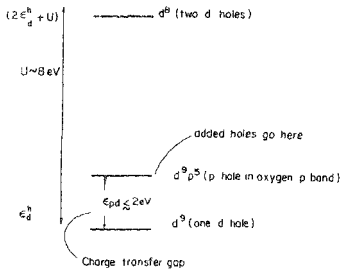


FIG. 2. The relevant energy levels of Cu and O ions in the plane.

## 2. Properties of cuprates

### 2.1. *Preliminaries*

The cuprates are layered compounds with conduction taking place in the [Cu $O_2$] layers. These layers are interspersed with rare-earth oxide and metal ions (Fig. 1). The parent compound $La_2CuO_4$ was first extensively studied by Rao and Ganguly[4] because it is an unusual example of a quasi-two-dimensional Mott insulator. Mott insulators are systems with an odd number of outer electrons per unit cell. According to one electron band theory of solids, such systems necessarily have a partially filled band of electronic states and ought to be *metallic*. Several three-dimensional transition metal oxides, *e.g.*, NiO, $V_2O_3$ ought to be metallic (for the same reason that Cu and Na are metallic) but are actually antiferromagnetically ordered insulators. $La_2CuO_4$ enlarges this class of electronically unusual materials in a new direction; the system consists of weakly coupled layers, *i.e.*, is quasi-two dimensional. We now briefly describe the relevant electronic-level structure of $La_2CuO_4$ and the effect of Sr doping. This provides us with the basic terms of description for this family of materials.

The relevant single-site energy levels of the [Cu $O_2$] unit cell are indicated in Fig. 2. The one d hole or $Cu^{2+}$ or $d^9$ level lies lowest, at energy $\epsilon_d^h$ with respect to the no-hole or $d^{10}$ configuration. To add another d hole ($Cu^{3+}$ or $d^8$) costs an extra energy ($\epsilon_d^h + U$), U( $\simeq$ 8eV) being the large single site or Mott Hubbard repulsion. The large value of U invalidates conventional noninteracting electron band theory, and leads to the stoichiometric one d hole per site material (*e.g.*, $La_2CuO_4$) being an insulator. The feature that distinguishes the cuprates as well as many transtition

metal oxides and chalogenides from model one band (d band) Mott insulators is the presence of oxygen p-hole levels $\epsilon_p^h$ *between* $d^8$ and $d^9$ energies, *i.e.*, *in* the correlation or Mott Hubbard gap. Thus the minimum energy required to transfer a d hole to an unoccupied site is $(\epsilon_p^h - \epsilon_p^d) \simeq 2eV$, the charge transfer being to the same site linear combination of $p_x$, $p_y$ oxygen hole orbitals with local $d_{x^2-y^2}$ symmetry. When holes are added to $La_2CuO_4$, *e.g.*, on replacing trivalent La with divalent Sr, they go into the oxygen p-hole band, and hop from site to site, both directly (with hopping amplitude $t_{pp} \simeq 0{\cdot}7ev$) and *via* admixture with d states ($t_{pd} \simeq 1e$ V). All the superconducting cuprates have a fraction x (with x ranging from 0·05 to 0·30) of mobile holes in the plane per $[CuO_2]$ unit cell. These systems are thus, generically, doped charge-transfer insulators[2] in the strong local correlation or Mott limit. I now summarize some of their properties, emphasizing their low-energy behaviour.

### 2.2. *The general phase diagram*

There is a change in the character of the $[CuO_2]$ system with doping. This is most clearly seen in the prototypical compound $La_{2-x}Ae_x$ Cu $O_4$, where Ae is an alkaline

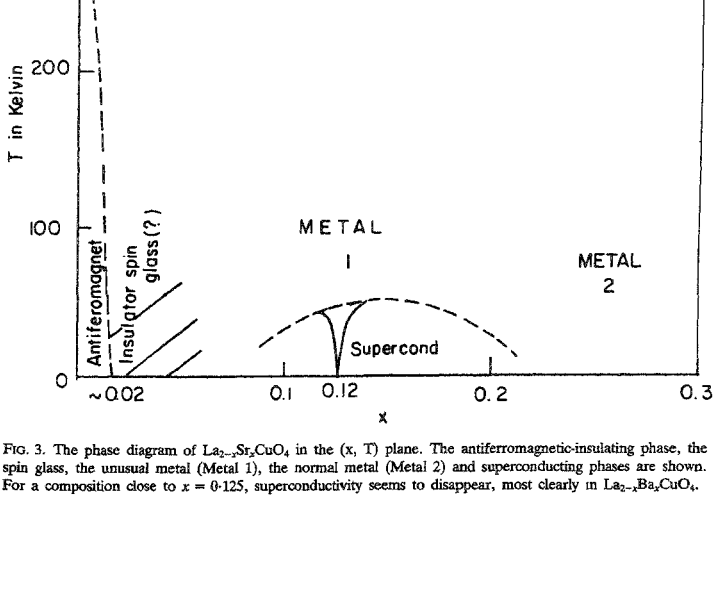


FIG. 3. The phase diagram of $La_{2-x}Sr_xCuO_4$ in the (x, T) plane. The antiferromagnetic-insulating phase, the spin glass, the unusual metal (Metal 1), the normal metal (Metal 2) and superconducting phases are shown. For a composition close to $x = 0{\cdot}125$, superconductivity seems to disappear, most clearly in $La_{2-x}Ba_xCuO_4$.

earth such as Sr or Ba. The phase diagram in the x–T plane is shown in Fig. 3. A number of striking features are evident. The antiferromagnetic order of $La_2CuO_4$ is destroyed extremely rapidly by doping, with $T_N$ falling from 210K to 0K as x changes from 0 to about 2%. Beyond this, there seems to be an insulating or barely metallic spin glass phase at zero temperature up to $x \simeq 0{\cdot}07$ or so. Other measurements in which x is carefully controlled and monitored seem to suggest[6] that the ground state is either insulating or superconducting; if the holes move, the insulating antiferromagnetic state is destroyed and a superconductor results. From $x \simeq 0{\cdot}07$ to 0·25, the ground state is superconducting, with $T_c$ increasing to a peak value of 40K ($x \simeq 0{\cdot}15$) and then decreasing. A recent and very intriguing observation[7] is the abrupt disappearance of superconductivity at a sharp value of $x \simeq 0{\cdot}125$. This narrow region with a new structure and highly reduced $T_c$ is most clearly seen in Ba-doped $La_2CuO_4$.

The normal metal region above $T_c$ is unusual in the entire range $0{\cdot}05 \lesssim x \simeq 0{\cdot}30$, with properties described below. Overdoped $La_{2-x}Cu_xO_4 (x \gtrsim 0{\cdot}25)$ seems a conventional metal as evidenced by low-temperature transport and Hall effect.

### 2.3. *Low-energy behaviour of metallic state*

The character of low-energy excitations in a quantum system depends directly on the nature of the ground state. These excitations can be probed thermally (*e.g.*, *via* change of free energy on heating). More selective probes include external perturbations such as electric and magnetic fields and random potentials due to impurities. The response of the system to such weak perturbations clearly depends on the nature of electronic excitations. We present here some electrical transport measurement results which strongly indicate that oxide metals are different qualitatively from other known ones.

Consider first the *ab*-plane dc electrical resistivity of cuprate superconductors above $T_c$ (Fig. 4). It is approximately linear in temperature over a wide range of several hundred degrees. The slopes are nearly the same ($\simeq 1\mu\Omega$ cm/K) to within a factor of two, for a wide range of clean single crystalline systems. The extrapolated zero temperature intercept can be very small: some layered compounds, *e.g.*., $Bi_2Sr_2CuO_6$ have very low $T_c$s $\lesssim$ 5K or no superconductivity depending on the hole-doping level (they seem to be on the overdoped side, *e.g.*., analogous to $x \gtrsim 0{\cdot}25$ in $La_{2-x}Sr_xCuO_4$). In these systems, the linear dependence is observed down to about 10K or so. Below 10K, due to some inevitable frozen randomness, there is a nonvanishing residual resistivity. Now a linear temperature dependence of resistivity, in the range $10K < T < 400K$, is unusual. For example, the resistivity of clean metals is due to electron–phenon interaction and rises initially as $T^n$ with $n$ ranging from 3 to 5. A number of other features, such as nonsaturation and large values at high temperature, make electron–phonon interaction an inconsistent possibility.

There are a number of properties generally consistent with the linear temperature dependence of resistivity[8]. Examples are the low-frequency background in Raman scattering, the ac conductivity $\sigma(\omega)$, the weakly temperature-dependent nuclear spin relaxation rate, etc. All of these imply that low-energy electronic excitations are not well defined, unlike conventional metals where they are.

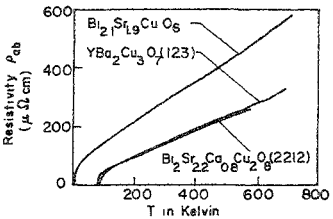


FIG. 4. The dc electrical resistivity of many-layered cuprates is shown as a function of temperature.

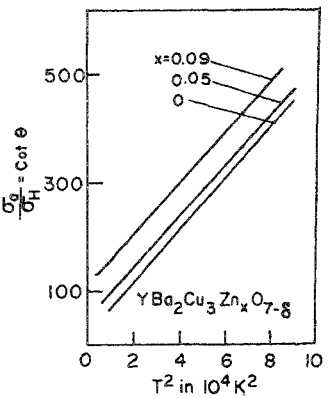


FIG. 5. The cotangent of the Hall angle, namely, the ratio of longitudinal to Hall conductivities for a number of Zn-doped $YBa_2Cu_{3-x}Zn_x$ systems is shown as a function of $T^2$ (from Chien *et al*[9]).

The Hall effect in the normal phase of the superconducting cuprates is also unusual[9]. It is strongly temperature dependent (*see* Fig. 5). For example, the ratio $(\sigma/\sigma_H)$ is proportional to $T^2$. Here, $\sigma$ is the electrical conductivity and $\sigma_H$ is the Hall conductivity. In a conventional metal, this ratio has the temperature dependence of $(1/\sigma) = \rho$ and so ought to go as T in our case. The $T^2$ dependence of this Hall angle is also seen in 123 compounds alloyed with Zn. This alloying reduces $T_c$ considerably, but the $T^2$ dependence is unchanged (*see* Fig. 5). An explanation for this $T^2$ dependence in terms of a new scattering mechanism has been proposed by Anderson[10].

Finally, we describe the unusual disorder effects[11] at low temperatures in $Bi_2\,Sr_2\,CuO_6$, which as mentioned earlier, has a linear resistivity ($\sim$ 140–150 $\mu\Omega$ cm) and no superconducting transition. At temperatures well below 5K, the inelastic processes are a small perturbation on the elastic random scattering of carriers, and weak localization effects are noticeable, *e.g.*, in the upturn of the resistivity (Fig. 6). There is a negative orbital magnetoresistance, which can be well fit to a weak localization form and from which one can extract an inelastic decay time for carriers (Fig. 7). This is the average time a carrier diffuses elastically before undergoing an energy-changing collision. The time is seen to go as $T^{-1/3}$, which is very short and has a new temperature dependence. The inelastic time in the pure system goes as $T^{-1}$. This strong enhancement of inelastic decay rates by disorder is unique, and if this relatively conventional analysis is to be believed, suggests that disorder has a very strong effect on quasi-particle propagation.

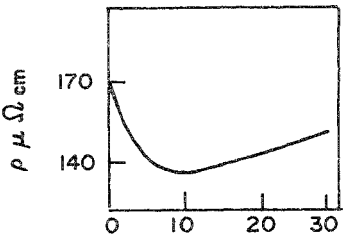


FIG. 6. Resistivity *vs* temperature for a clean $Bi_2Sr_2CuO_6$ specimen.

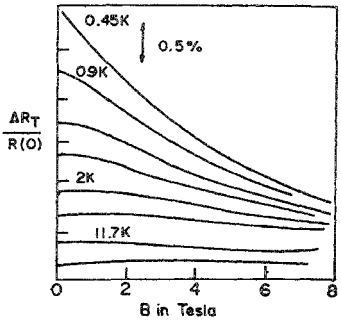


FIG. 7. The fractional negative magnetoresistance $[\Delta R_T/R(O))]$ of $Bi_2Sr_2CuO_6$ as a function of magnetic field and temperature (from Jing *et al*[11]).

The main message from all these results is that the lowest-energy ($\epsilon \lesssim 0{\cdot}01$ ev) electronic excitations in cuprates are unlike those of any known metal. It is increasingly believed by many that the key to high-temperature superconductivity is in understanding these unusual normal state properties[12]. There have been many attempts at this, some of which I briefly review. I then pose the problem of the correct description of these systems in several different ways.

### 3. Ideas and theories

Superconductivity in the oxides is due to coherence between electron *pairs*. This is confirmed by experiments which show that the magnetic flux threading a superconductor is quantized in units of (hc/2e). The presence of pairs is signalled by the occurrence of (2e) in the denominator. There is widespread disagreement however on what causes pairing. In conventional superconductors, pairing is due to retarded phonon-induded attraction. There is no evidence for a large electron-phonon coupling in cuprates making a high $T_c$ possible. Therefore, theories of cuprate superconductivity fall into two classes. In the more conventional approaches, one looks for other bosonic excitations which have the right energy scale and coupling to electrons so that a high $T_c$ is possible. The metallic state is conventional. Bosonic candidates include excitons, plasmons, magnons, spin fluctuations, etc. This kind of system almost always has a normal metallic state above $T_c$ unless radical assumptions are made about the boson spectrum and the electron–boson coupling. In the other classes of theories, it is assumed that because of strong local correlations as well as quantum dynamics and statistics, novel ground states arise. We shall briefly consider some approaches of this type here.

The earliest, most-sustained and far-ranging ideas in this field are due to Anderson[12,13]. He argued, very early after the discovery of high $T_c$, that the latter was a strong correlation effect connected with the formation of a coherent assembly of singlet spin pairs, the latter being possible only for strong correlation. The quantum mechanical overlap of a large number of such singlet configurations with different pair lengths and pair members gives such a resonating valence bond (RVB) state special stability. Doping the RVB system with holes leads to two kinds of excitations, neutral spin-like ones (spinous) and charged hole-like ones (holons). The real question pertains to the degree to which these mutually interacting excitations are well approximated by relatively weakly coupled spinons and holons. To proceed further, an explicit Hamiltonian is needed, the simplest being the one-band Hubbard model.

The one-band Hubbard model describes correlated electron hopping on a lattice. It is given by

$$H = \sum \epsilon_i n_{i\sigma} + \sum t_i \, a^+_{i\sigma} \, a_{j\sigma} + U \sum n_{i\uparrow} \, n_{i\downarrow}.$$

Here $\epsilon_i$ is the energy of one electron at site $i$ and $t_{ij}$ is the amplitude of hopping from site $i$ to site $j$, $U$ the one site or Hubbard correlation energy. This term describes the extra (coulomb) energy cost of putting two electrons on the same site. If $U$ is large, such two-electron configurations are disfavoured; in the cuprate example, this corresponds to the two-*hole* configuration $d^8$, which has an energy $2\epsilon + U$. For large $U$, the properties of the Hubbard model system depend strongly on filling. At one electron per site, the system is a Mott insulator with electrons localized at parent sites and with nearest neighbour spins coupled antiferromagnetically. This corresponds to $La_2CuO_4$. Doping with holes introduces, in reality, holes in the Oxygen p band. Each such hole (spin 1/2) is strongly and antiferromagnetically coupled to a copper $d^9$ spin in the vicinity, and the two form a singlet. This composite singlet can be thought of as a spinless hole in the Hubbard band. Thus, as first pointed out by Zhang and Rice[14], the more realistic two-band (oxygen *p*-copper d band) model reduces, in the limit of low doping, to a one-band Hubbard model. We now discuss this model further.

A number of authors have proposed various kinds of spin-liquid ground states, depending on the spin-pairing amplitudes and relative phases. Some widely discussed possibilities are the uniform RVB phase, the spiral, chiral and flux phases, etc. One common strategy is to look for possible spin-liquid solutions in the *undoped* Mott insulator phase (the actual ground state solution is a Neel antiferromagnet) and hope that they describe the actual spin–liquid ground states in the *presence* of holes[15]. A common formalism for various spin–liquid possibilities uses a composite field description, the physical fermion being a composite fermion boson field $= f^+_{i\sigma} \, b_i$. Thus, $f^+_{i\sigma}$ describes a spin $\sigma$ fermionic excitation, and $b_i$ the destruction of a (bosonic) hole at site $i$. A site has either a spin or a hole:

$$f^+_{i\sigma} \, f_{i\sigma} + b^+_i \, b_i = 1. \qquad (1)$$

This local constraint is hard to implement exactly and independently at each site. Most often the constraint is satisfied on the average. The local fluctuations from the average can be thought of as gauge fields which develop characteristic dynamics because of the coupling induced between Fermi and Bose fields. These gauge fluctuations can give rise to long-range interactions and sometimes, fractional statistics for electrons.

The general one-band Hamiltonian in the strong correlation limit is described as the sum of a hopping term $t_{ij}$ and an antiferromagnetic spin-exchange term $J_{ij}$, *i.e.*,

$$H_{t-J} = \sum_{i,j,\sigma} t_{ij} f^{+}_{i\sigma} b_i f_{j\sigma} b^{+}_j + \sum_{i,j} J f^{+}_{i\alpha} (S)_{\alpha\beta} f^{+}_{i\beta} \cdot f^{+}_{j\gamma} (S)_{\gamma\delta} f_{i\delta}. \tag{2}$$

The uniform RVB corresponds to assuming the singlet amplitude $\langle f^{+}_{i\alpha} f_{j\beta} \rangle$ being a nonzero constant. Fluctuations with respect to this mean are described by a gauge field. Its dynamics is determined by its coupling to the Fermi and Bose fields, and turns out to be diffusive. The coupling between current-carrying Bose and Fermi excitations and the guage field leads to the observed normal state transport properties, under several further assumptions[16]. The main difficulty with this kind of theory is that Bose fields condense. In the condensed phase, the system is easily shown to be a normal Fermi liquid. There are many suggestions proposed to suppress Bose condensation.

I now describe the problem of a doped-correlated metal from three points of view. One can argue that the theoretical problem is one of using too many basic fields. In reality, one has just electrons (or holes) correlating their motion to avoid each other. The correlation effect is described in terms of two fields, a fermion and a boson field, with a constraint to account for the overcompleteness. The constraint itself leads to another degree of freedom which couples fermions and bosons. It is not clear that a correlated fermion field can only be described as three coupled fields, one of which has a tendency to condense. Another way of looking at the problem of a doped Mott insulator is to view it as one of local magnetic moments disappearing on doping. One is familiar with the disappearance of local moments due to the Kondo effect, *i.e.*, antiferromagnetic coupling of the local moment to the conduction electron moment. Due to the repeated spin flips caused by this coupling, the moment disappears, at temperatures exponential in the coupling. In a doped Mott insulator, *e.g.*, one described by eqn (2), the exchange interaction $J_{ij}$ produces coherent, coupled motions of spins. The charge fluctuations $t_{ij}$ destroy local spin memory because the hopping motion of a hole causes a spin to diffuse. The energy scales to compare are $J$ and the effective hopping energy $\delta t$ where $\delta$ is the hole density. Around this hole density, spins dont stay at a site long enough to interact with a diffusing neighbour, so that models with well-defined spins are inadequate. One has long-lived magnetic fluctuations, charge fluctuations and electrons coupled to these. We do not know how to describe these well.

A third, rather formal view of the problem is as one of minimal relevant fields

and symmetries[17]. The two local fields acting on a spin 1/2 particle are a magnetic field $\vec{m}_i(\tau)$ which couples to the local spin $\vec{S}_i$ and the local potential which couples to the local density $(n_i-1)$. In the zeroeth approximation, for strong correlation, there are independent magnetic moments at each site, *i.e.*, there is a large-field $\vec{m}_i$ and the energy does not depend on the spatial orientation of this. Thus there is a local SU(2) invariance of the energy with respect to possible local spin directions. This SU(2) invariance is broken by the exchange-coupling $J_{ij}$. Further, if there are no charge fluctuations, as happens for the half-filled Hubbard model in the strong correlation limit (Mott insulator), there is an electron hole symmetry which leads to local SU(2) invariance in the space of the operators $(c_{i\uparrow}, c^{+}_{i\downarrow})$. This invariance is broken for half filling in the metallic state and always away from half filling, by the deviation $\delta$. With both of these gauge invariances, one can associate local fields. The problem is one of the dynamics of these gauge fields, coupled to electronic degrees of freedom. The problem of the Mott transition, for instance, can be thought of as one where the latter gauge field (charge field) is massless in the metallic phase and develops a mass in the insulating phase. In the doped Mott insulator, the longitudinal fluctuations are massless, but the transverse ones are not. Thus it appears that an understanding of this novel gauge field model could provide the basis for a microscopic theory of strongly correlated lattice systems.

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