PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Electronic Structure of the High T$_{\text{c}}$ Superconductors [and Discussion]

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Phil. Trans. R. Soc. Lond. A 1991 **334**, 459-471
doi: 10.1098/rsta.1991.0026

Electronic structure of the high T_c superconductors

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The high T_c superconductors have one structural element in common, namely CuO_2 planes which are lightly doped away from an average valence of Cu^{2+}. In the absence of this doping the planes are in a Mott insulating state with local $S = \frac{1}{2}$ moments on each Cu-site. There is considerable evidence both experimental and theoretical supporting the assignment of the extra holes, introduced by doping, to the antibonding O 2p-orbitals. The strong hybridization between these orbitals and the central Cu 3d-orbitals makes it favourable to bind the extra hole with a Cu^{2+} local moment to form a spin singlet state centred on a CuO_4 square. This singlet, however, is mobile and the combination of mobile charged singlets and local spins is described by the so-called t–J model. This has a number of consequences which can be tested experimentally. For example, one can use this model to estimate the hyperfine coupling constants which are measured in NMR experiments. The prediction that the only spin degrees of freedom are the local Cu^{2+} spins even upon doping can also be tested in NMR experiments.

1. Introduction

The discovery of high-temperature superconductivity in the cuprate oxides (Bednorz & Müller 1986) has been without doubt the most exciting and unexpected development in solid state physics in the past decade. Further this discovery poses the most urgent problem to the theory of solids. What is so special about this small group of compounds that causes them to be superconducting at temperatures *ca.* 10^2 K? Naturally to begin to answer this question we need to understand the relevant electronic structure at low energies. This in turn is determined by the bonding pattern and the crystal structure.

The cuprate materials are complex materials with large unit cells but they have a single common active element namely CuO_2 planes with four-fold coordinate Cu atoms and two-fold coordinated O atoms. When these materials are prepared so that the formal Cu-valence is $2+$ and O-valence is $2-$, the CuO_2 are magnetically ordered (Mott) insulators at low temperatures. Superconductivity arises when the counter ions are changed slightly so as to raise the formal valence of the copper ions to $Cu^{2+\delta+}$ with $\delta \approx 0.2$. This change is accompanied by only slight changes in the Cu–O bond lengths and no essential change in the Cu–O bonding pattern as determined by the crystal structure. This tells us right away that the electronic structure must evolve in a continuous way away from the Mott insulating state. Any real change in the

electronic structure requires a change in the bonding pattern which in turn must show up in the crystal structure. Yet the crystal structure of the key CuO_2 plane evolves slowly and continuously. This fact alone argues that we are dealing with a doped Mott insulator.

Right at the outset of this problem, this idea was used by Anderson (1987*a*, *b*) to propose that the solution to the high T_c problem lies in the study of strongly correlated electrons near the Mott insulating state and that the simplest model of this case, namely a one-band model, would suffice to understand the physics of this type of quantum fluid. In spite of a tremendous effort in the past years our understanding of this problem is far from complete (e.g. see the recent Los Alamos conference (Bedell *et al.* 1990)). This talk will concentrate on the simpler questions concerning the reduction of this complex electronic system to the one-band model. First we review the line of reasoning connecting the larger energy scale and larger electronic model to the reduced one-band model at the low energy scale. Secondly a comparison can be drawn with the predictions of this model and various experiments. Nuclear resonance techniques are powerful probes of electronic structure on the low energy scale and give us sensitive tests on the low energy scale of the assumptions in the one-band model. Further tests can be made using high energy spectroscopy particularly, X-ray absorption and electron energy loss spectroscopies.

2. Electronic structure of the CuO_2 planes

It is generally accepted that a good starting point to describe the CuO_2 planes is a multiband model composed of $3d_{x^2-y^2}$ orbitals on the Cu-sites and $2p_{x,y}$ orbitals on the O sites (Emery 1987). This gives a model hamiltonian with no fewer than five orbitals per unit cell and when we include the various interatomic (U_{pd}) and intraatomic (U_d, U_{pp}) Coulomb forces in each unit cell we arrive at the following hamiltonian (in hole notation relative to a filled shell ($3d^{10}, 2p^6$) configuration)

$$\begin{aligned} H = &\sum_{i\sigma} \epsilon_d\, d^+_{i\sigma} d_{i\sigma} + \sum_{lm\sigma} \epsilon_p\, p^+_{lm\sigma} p_{lm\sigma} + \sum_{\langle i;lm\rangle} t_{pd\sigma}\, p^+_{lm\sigma} d_{i\sigma} + \text{h.c.} \\ &+ \sum_{\langle l,m;l',m'\rangle} t_{pp}\, p^+_{lm\sigma} p_{l'm'\sigma} + \text{h.c.} + \sum_i U_d\, n_{i\uparrow} n_{i\downarrow} \\ &+ \sum_{\substack{\langle i;lm\rangle \\ \sigma\sigma'}} U_{pd}\, n_{lm\sigma} n_{i\sigma'} + \sum_l \sum_{m\sigma\neq m'\sigma'} U_{pp}\, n_{lm\sigma} n_{lm'\sigma'} \end{aligned} \tag{1}$$

with $d^+_{i\sigma}$ as the creation operator for a hole in a $3d_{x^2-y^2}$ state on Cu, $p^+_{lm\sigma}$ for a hole in a $2p_{x(y)}$ state on O, etc.

This is a very complicated hamiltonian with many parameters. Depending on the values of these parameters, different limiting behaviours can occur at low energies. Various methods have been used to estimate the values of the parameters that enter equation (1). Because the Mott insulating state cannot be described by direct application of density functional theory, new techniques have been devised to make use of the strengths of the density functional method in estimating total energies and densities and from them to obtain parameter values. The values obtained in this way (see, for example, Hybertsen *et al.* 1989; McMahon *et al.* 1989) are typical and are quoted in table 1. These values also agree with early empirical estimates by Mila (1988) and a recent more extensive analysis by Eskes & Sawatzky (1990) (see table 1).

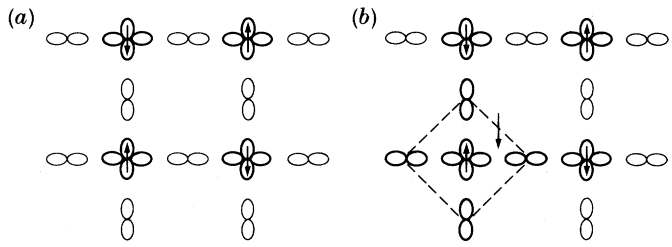

Figure 1. A schematic representation of electronic structure of undoped (*a*) and the hole doped (*b*) CuO_2 plane.

Table 1. *Parameters of the multiband hamiltonian* (1)

(All energies are in electronvolts. The energy parameters in the multiband hamiltonian (1) obtained from constrained local density calculations (first column) and empirical values (second column).)

	Hybertsen *et al.* (1989)	Eskes & Sawatzky (1990)
$\epsilon_p - \epsilon_d$	3.6	2.75–3.75
$t_{pd\sigma}$	1.5	1.5
t_{pp}	0.65	0.65
U_d	10.5	8.8
U_d	4	6
U_{pd}	1.2	< 1

If we look at table 1, the largest Coulomb interaction is the on-site interaction between d-electrons on Cu sites, U_d, and the largest hopping integral is that for the σ-bond between a $3d_{x^2-y^2}$ Cu orbital and a neighbouring $2p_{x(y)}$ O orbital, $t_{pd\sigma}$. If we simplify to these terms only, i.e. set $t_{pp} = U_p = U_{pd} = 0$ and notice that $t_{pd\sigma}/(\epsilon_p - \epsilon_d)$ ($\approx \frac{1}{3}$) is rather small, we can make a perturbation theory in this parameter (Zhang & Rice 1988). First for the case of exactly 1 hole per Cu, i.e. a formal valence of Cu^{2+}, then this hole will sit primarily in a $3d_{x^2-y^2}$ orbital and have some hybridization with the neighbouring 2pO orbitals through the $t_{pd\sigma}$ term. Note it is this strong hybridization that determines the CuO_2 planar structure. It is straightforward to estimate the Heisenberg nearest neighbour (NN) exchange coupling using Anderson superexchange theory. The result in perturbation theory is

$$J = 4t_{pd\sigma}^4/(\epsilon_p - \epsilon_d)^2 U + 4t_{pd\sigma}^4/(\epsilon_p - \epsilon_d)^3. \quad (2)$$

In this case the low energy hamiltonian is simply a Heisenberg spin hamiltonian. There is a clear separation between charge excitations which have a gap and the spin excitations described by the Heisenberg term. Recently Hybertsen *et al.* (1990) went further and by fitting to results of an exact diagonalization of the hamiltonian (1) on small clusters to a Heisenberg model, they could extract a value of J including all terms in equation (1). Their value of $J = 0.13$ eV agrees well with experimental estimates. The electronic configuration is sketched in figure 1*a*.

The corrections to an NN Heisenberg hamiltonian are estimated to be small. For example, the next nearest neighbour term is estimated to be only of order $10^{-2}\,J$. Similarly the Dzyaloshinskii–Moriya interaction which occurs in the presence of slight distortions away from the ideal CuO_2 planar structure is of this order of

magnitude too (Coffey *et al.* 1990). Schmidt & Kuramoto (1990) have suggested a large four-site term but this suggestion has lacked experimental confirmation up till now.

While the description of the Mott insulator is more or less agreed upon, there has been much more controversy about the effect of doping. It is clear, however, that, with parameter $U_d > \epsilon_p - \epsilon_d$, the added holes in the hole doped materials must go primarily into O orbitals. The question then is whether this will require a multiband description such as the multiband hamiltonian (1) proposed by Emery (1987), or whether it can still be reduced to single band hamiltonian as Anderson proposed (1987*a*, *b*).

If we start with a simplified version of (1), retaining only the U_d and $t_{pd\sigma}$ terms as the most important ones, then progress can be made by treating the ratio $t_{pd\sigma}/(\epsilon_p - \epsilon_d)$ as a small parameter in perturbation theory. First we consider a single Cu-ion with its four O-neighbours. When we place two holes on this square complex and seek to maximize the gain from the hybridization energy, $t_{pd\sigma}$, it is immediately clear in second-order perturbation theory, that this is achieved by placing the second hole in a combination of the O p-orbitals with the same symmetry as the central $3d_{x^2-y^2}$ orbital and also by forming a spin singlet. This is illustrated in figure 1*b*. This state as shown by Zhang & Rice (1988), obtains a binding energy relative to the non-bonding state of

$$E_{\text{singlet}} \approx -8t_{dp\sigma}^2\left(\frac{1}{\epsilon_p - \epsilon_d} + \frac{1}{U + \epsilon_d - \epsilon_p}\right). \tag{3}$$

This strong binding suggests immediately that the low energy properties will be governed by these singlets. Note, however, that the singlet state on one CuO_4 has a considerable overlap with that on neighbouring squares (there is a O-site common to both) so that there will be a substantial NN hopping term (*ca.* $-1.5t^2/(\epsilon_p - \epsilon_d)$) in perturbation theory. In the dilute limit of hole doping the charge will be carried by the tightly bound singlets moving in the $S = \frac{1}{2}$ background which in turn are coupled by a Heisenberg term. This gives us the t–J hamiltonian

$$H_{t-J} = \sum_{\langle ij\rangle\sigma} t_{ij}(1 - n_{i-\sigma})\, d^+_{i\sigma} d_{j\sigma}(1 - n_{j-\sigma}) + \text{h.c.} + J \sum_{\langle ij\rangle} \boldsymbol{S}_i \cdot \boldsymbol{S}_j, \tag{4}$$

where the sum over i, is restricted to Cu sites. This is the same form as one obtains from a one-band Hubbard model in the case of dilute doping away from half-filling and in the limit $t/U \to 0$. In this limit of the Hubbard model the ratio $J/t \ll 1$, but in the present case one should treat this ratio as a material parameter, to be determined.

A similar result was obtained by Eskes & Sawatzky (1988). They treated the hamiltonian (1) as having the periodic Anderson model form with the d-states as the strongly correlated atomic states and the p-states as forming the equivalent of the conduction band states. They solved first for a single Cu atom in the O network and showed that a singlet A_{1g} state was formed. The motion of this singlet through the lattice is then described through the t–J model. In contrast to usual heavy fermion materials, we are in the limit here where the singlet binding energy exceeds the Fermi energy of the carriers.

The reduction of the multiband description (1) to the single-band t–J model, is not controlled by a small parameter (e.g. the same physical quantities enter the binding and dispersion of the singlet). This has led to considerable discussion in the literature on the validity and limitations of the reduction from multiband to one-band models

(see, for example, Emery & Reiter 1988, 1990; Gooding & Elser 1990; Zhang & Rice 1990*a*, *b*; Shastry 1989). There are interesting questions but of most relevance is the question how good is the reduction in the realistic case when we start with the full hamiltonian (1) and use the parameters in table 1. Recently, Hybertsen *et al.* (1990), have used a cluster method to tackle this problem. They solved the full hamiltonian (1) on a finite cluster of five Cu and 16 O atoms and compared the low energy spectrum with that obtained with the t–J model. They found a good fit between the two spectra both as to the number, degeneracies and energy splittings when they added a t' term, describing next nearest neighbour hopping of the singlet. Their parameters are

$$t = 0.44\,\text{eV}; \quad t' = -0.06\,\text{eV}; \quad J = 0.13\,\text{eV}. \tag{5}$$

Their values have the ratio $J/t < 1$ but not arbitrarily small and the ratio t'/t is also finite.

3. Nuclear resonance studies of the electronic structure

Nuclear resonance techniques are powerful tools to study the low energy electronic structure. In particular they offer site specific probes of the spin densities and through the hyperfine coupling constants of the nature of the electronic wave functions. This is especially true in the case of the cuprate superconductors which have large unit cells with different atomic sites. On the other hand we have discussed above the case that a simplified one-band model is the operative model at low temperatures. In this model the only spin degrees of freedom are Cu^{2+}-moments so that this model can be very directly tested by nuclear resonance methods.

Let us consider the case of the $YBa_2Cu_3O_{7-x}$ compound series since that is the best studied. In particular detailed studies have been made on the ^{63}Cu, ^{17}O and ^{89}Y nuclei and the results have been summarized by Walstedt & Warren (1990). The key assumption made above was that Cu^{2+} ions behave as local $S = \frac{1}{2}$ moments. From this it follows at once that the onsite hyperfine hamiltonian coupling the nuclear and electronic spins has the form

$$H^{(1)}_{\text{hyp}} = \sum_i {}^{63}\boldsymbol{I}_i \cdot A \cdot \boldsymbol{S}_i, \tag{6}$$

where the A coefficients are to be estimated by a comparison to various Cu salts. Since the electronic spin resides in a $3d_{x^2-y^2}$ orbital there is no contact term and the A term is composed of a series of contributions from core polarization, dipole interactions and spin-orbit terms. The resulting hyperfine interactions are anisotropic because of the planar structure. Mila & Rice (1989) estimated the following values for $A_\parallel$ (parallel to the c-axis) and $A_\perp$ (in the ab-phase)

$$A_\parallel \approx 230\,\text{KOe}/\mu_B; \quad A_\perp \approx 5\,\text{KOe}/\mu_B. \tag{7}$$

It is impossible to fit the data with such a form and an examination of the structure of CuO_2 planes shows that the well-known phenomenon of transferred hyperfine interaction should be present here. Mila & Rice (1989) did a chemical analysis of the transferred hyperfine interaction and found the leading contribution came from the coupling of a Cu^{2+} electronic spin through σ-overlaps with the O neighbour to a neighbouring 4s-state which in turn has a strong onsite contact interaction with the Cu nuclear spin at that site. In this way a transferred hyperfine interaction occurs between the localized Cu electronic spin on a site and the nuclear spin on a

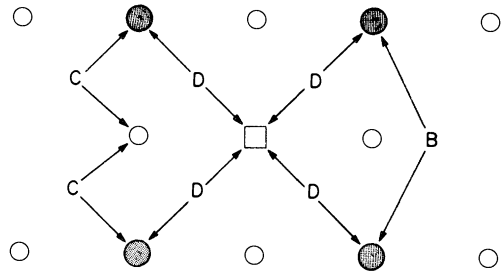

Figure 2. The transferred hyperfine couplings that occur through the 2p-orbital between the Cu^{2+} electronic spins and the ^{63}Cu (B), ^{17}O (C) and ^{89}Y (D) nuclei. ○, O; ●, Cu; □, Y.

Table 2. *Hyperfine parameters for* ^{63}Cu *nuclei*

(All constants in units KOe/μ_B. Hyperfine parameters for ^{63}Cu (2) nuclei in $YBa_2O_3O_7$. The first column gives the values estimated using a chemical analysis (Mila & Rice 1989). In the second, third and fourth columns recent experimental values are quoted.)

	Mila–Rice (1989)	Barrett *et al.* (1990)	Walstedt–Warren (1990)	Imai (1990)
$A_\perp$	5	19	−11	37±5
$A_\parallel$	−228	−214	−188	−158±2
B	40	38	45	39±1
$A_\perp+4B$	165	171	167	195±9
$A_\parallel+4B$	−68	−62	−10	0±4

neighbouring site as illustrated in figure 2. The resultant hyperfine hamiltonian has the form

$$H^{(2)}_{\mathrm{hyp}} = B\sum_i\sum_\tau {}^{63}\boldsymbol{I}_i\cdot\boldsymbol{S}_{i+\tau}, \tag{8}$$

where the sum runs over NN Cu-sites. Mila & Rice (1989) made an estimate of the size expected for the coefficient B and obtained a value $B\approx 40\ KOe/\mu_B$. Since it derives from a contact interaction, it is isotropic in spin space.

This form of the hyperfine hamiltonian can be directly tested. First of all through the Knight shifts $^{63}K_\mu$ which take the form ($\hbar=1$)

$$^{63}K_\parallel = (A_\parallel+4B)\,\chi_0/2\mu_B\,{}^{63}\gamma_n;\ {}^{63}K_\perp = (A_\perp+4B)\,\chi_0/2\mu_B\,{}^{63}\gamma_n, \tag{9}$$

where $^{63}\gamma_n$ is the ^{63}Cu nuclear moment, μ_B the Bohr magneton and χ_0 the spin susceptibility. Many workers (see Walstedt & Warren 1990) have reported that the Knight shift $\|c$-axis is very small, essentially zero. This finds a natural explanation in this approach since the combination $(A_\parallel+4B)$ that enters involves an almost complete cancellation between the two terms. For field orientation in the basal plane, it is necessary to have an estimate of χ_0, the spin susceptibility (assumed isotropic in view of the small spin-orbit couplings in Cu ions), to obtain values of the hyperfine constants from the experimental Knight shifts. This leads to some uncertainty in the experimental values. In table 2 we summarize the estimated values, together with those obtained by a detailed analysis of experiments by various groups.

In view of the uncertainties in the parameters the agreement between the theoretical estimates and the experimental values is very satisfactory. Since these hyperfine coupling constants are sensitive to the detailed electronic structure, it is clear that this description which starts from the ionic point of view and treats the

hybridization effects perturbatively must be quite good. If there had been substantial changes in the nature of the electronic states then we would expect to see this reflected sensitively in the hyperfine coupling constants.

A second test concerns the doping dependence of the hyperfine constants. Since the $x = 0$ compounds have a substantial hole concentration the question arises what happens when we pass through $x \approx 0.4$ (the 60 K superconductors) to the $x = 1$ case which is an ordered magnetic insulator without hole doping. Again we can ask if there are substantial shifts. The first case that is easy to investigate is the cancellation in the c-axis Knight shift. Since at $x \approx 0.4$ $\chi_0(T)$ develops a strong temperature dependence in the normal state (unlike the case of $x = 0$ which is temperature independent), any change in this cancellation will be easily observed. In fact $K_{\parallel}(T)$ is essentially temperature independent showing that this sensitive cancellation continues in the $x \approx 0.4$ state (see, for example, Walstedt & Warren 1990).

Another independent test of the hyperfine interactions comes from the observation of the antiferromagnetic zero field nuclear resonance. Yasuoka *et al.* (1988) observed this resonance in the $x = 1$ insulator and from their frequency they determine the combination

$$\mu_{\text{eff}} |A_{\perp} - 4B| = 80k \text{ Oe}, \tag{10}$$

where μ_{eff} is the AF ordered magnetic moment. If we take a value $\mu_{\text{eff}} \approx 0.6\,\mu_{\text{B}}$ in agreement with experiment and with theoretical estimates of the ordered moment for $S = \frac{1}{2}$ Heisenberg models in two dimensions, then this yields a value of $|A_{\perp} - 4B| \approx 130$ KOe/μ_{B} which we can see from table 1 is in good agreement with the estimates made from the high T_c conductor with $x = 0$. So we come to the conclusion that there is a high degree of consistency in the Cu hyperfine parameters obtained in conducting samples even with different hole concentrations and in insulating samples. Further the values are quite in the expected range for a model of localized Cu^{2+} spins primarily in $3d_{x^2-y^2}$ orbitals. These results speak strongly against a collapse of the local correlation gap upon doping or a collapse of the charge transfer gap either.

This one-band model can be more severely tested by looking at the hyperfine couplings and nuclear resonance on other nuclei. Particularly the ^{17}O nuclei and the ^{89}Y nuclei are good probes and the latter have been studied extensively by Alloul and coworkers (1989). The ^{89}Y nuclei are clearly coupled to the O orbitals through a transferred hyperfine interaction rather than directly to the Cu orbitals which are too far away to overlap substantially. The key assumption in the analysis presented earlier is that the extra holes which are introduced upon doping lie in the σ-bonding O orbitals and are strongly hybridized into local singlets so that the magnetic response is controlled only by the Cu^{2+} spins. This assumption has a clear consequence for the way the resonance properties on the O and Y nuclei should behave. Their response should arise from a transferred hyperfine coupling to the Cu spins and take the form

$$H^{(3)}_{\text{hyp}} = C \sum_{n,\delta} {}^{17}\boldsymbol{I}_n \cdot \boldsymbol{S}_{n+\delta}, \quad H^{(4)}_{\text{hyp}} = D \sum_{n,\delta} {}^{89}\boldsymbol{I}_n \cdot \boldsymbol{S}_{n+\delta}, \tag{11}$$

where the sum over δ runs over the nearest neighbour Cu sites of an O or Y nucleus (see figure 2). This leads at once to the result that the Knight shift observed on the O or Y nuclei should be directly proportional to the spin susceptibility χ_0,

$$^{17}\text{K} = C\chi_0/{}^{17}\gamma_n\mu_{\text{B}}; \quad {}^{89}\text{K} = 4D\chi_0/{}^{89}\gamma_n\mu_{\text{B}}. \tag{12}$$

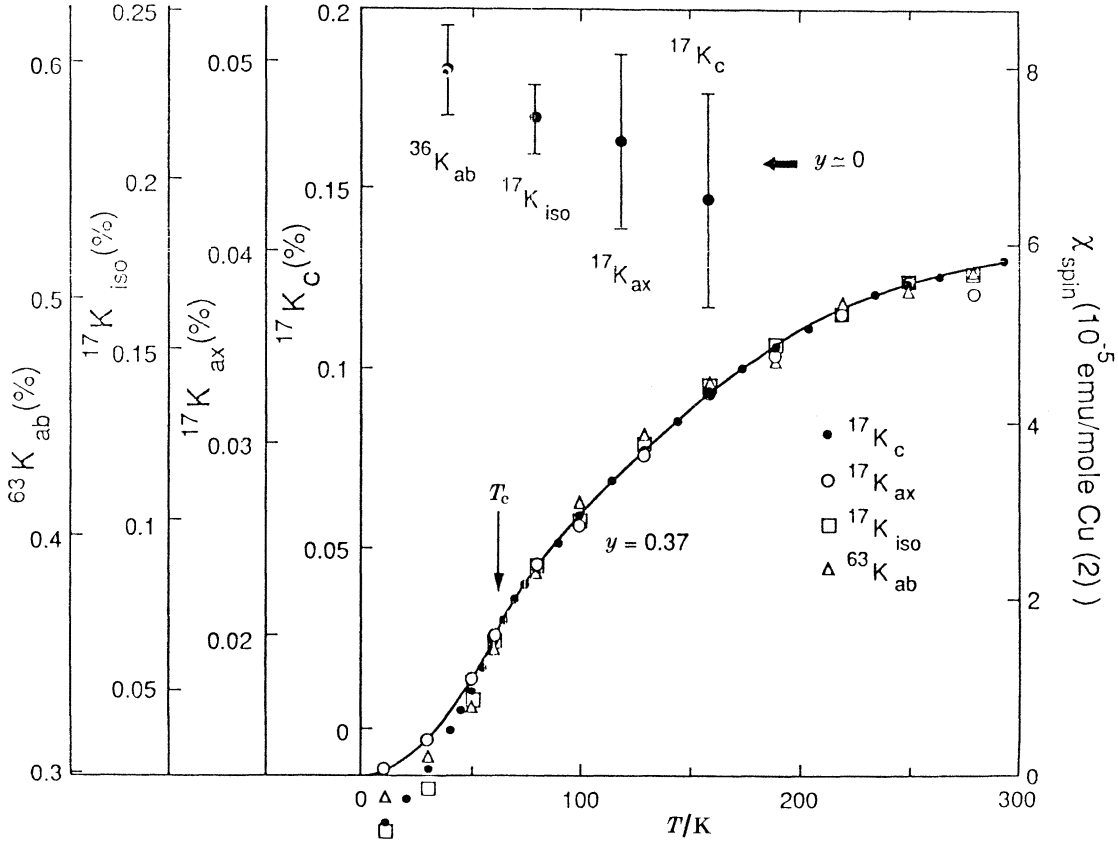

Figure 3. Various components of the Cu and O Knight shifts in $YBa_2Cu_3O_{6.63}$ are plotted against temperature with different vertical scales and origins. The T-independent values of the spin Knight shifts in the $x = 0$ material (i.e. $YBa_2Cu_3O_7$) are also plotted with the same vertical scales. This figure is reproduced from Takigawa *et al.* (1991).

In the case of $x = 0$, since $\chi_0(T)$ is independent of temperature, this is not a very stringent condition. However, for lower doping this condition is much more strict since $\chi_0(T)$ develops a strong temperature dependence even in the normal state. In figure 3 we show the recent results of Takigawa *et al.* (1991). This shows clearly that there is a clear proportionality between the Knight shifts $^{63}K_{\perp}(T)$ on Cu sites, $^{17}K(T)$ on O sites, $^{89}K(T)$ on Y sites and the bulk susceptibility. This is a clear test of the hypothesis that there is a single quantum fluid of strongly hybridized Cu and O orbitals and not two fluids with separate localized Cu spins and itinerant O holes. The latter hypothesis requires a separate contribution particularly on O sites with its own temperature dependence which is in contradiction to the results shown in figure 3. Note, however, that this conclusion is contested by the Grenoble group (Butuad *et al.* 1989; Berthier *et al.* 1990).

The hyperfine hamiltonian (11) for the ^{17}O nuclei describes a purely isotropic Knight shift. In fact a small anisotropy was observed and analysed by Takigawa *et al.* (1989). They showed that it is consistent with a spin density in the σ-bonding 2p-orbitals. This is again consistent with the bonding picture presented above and a further confirmation of the role of the pdσ-hybridization in these compounds.

The relaxation rates of the nuclear resonances are also an important tool to study

the low frequency magnetic responses of the quantum fluid. However, we shall not go into these questions and just remark that recently quite detailed analyses of the temperature dependences of these rates have been made (Millis *et al.* 1990; Monien *et al.* 1991*a*, *b*), using a phenomenological form for the wavevector and frequency dependent susceptibility. The very different temperature dependences observed on Cu and on O or Y sites find a natural explanation in terms of predominantly antiferromagnetic fluctuations which are picked up by the Cu nuclear spins but which cancel out at O or Y sites.

4. High energy spectroscopies

There have been many experimental investigations of the cuprate superconductors and we do not attempt a summary of all results. Instead we focus on the question of evidence for the persistence of strong onsite correlations even into the doped materials. Two recent sets of experiments which address this question directly are the electron energy loss spectroscopy (EELS) experiments by Romberg *et al.* (1990) and X-ray absorption spectroscopy (XAS) experiments by Chen *et al.* (1991). Both these experiments in principle measure the same quantity namely the density of states to promote an electron from the filled 1s O core state to an empty 2p-state. In the insulating compounds the empty 2p-states arise due to hybridization of the Cu^{2+} ions with the O neighbours and a low energy peak is found which can be ascribed to this process.

The most interesting results then occur upon hole doping since then one introduces the formal Cu^{3+} sites which are the spin singlets. A new process can now occur in which the excited electron is injected into this state to form a formal Cu^{2+} state. This new process should occur in proportion to the hole doping and an important test of the strong correlation limit, is the question of whether this appears as a separate peak at low energies or merely a broadening of the existing peak. In fact both groups report similar results which show a separate peak growing with hole doping with an energy separation *ca.* 2 eV. A detailed analysis has been made by Hybertsen *et al.* (1990), using the multiband hamiltonian (1) with the parameter values in table 1. They calculate the spectra using a cluster approximation and obtain excellent agreement for the splitting and intensity of the peaks. Since as one discussed earlier, the hamiltonian (1) reduces at low energy to a strongly correlated single-band model, these results are further confirmation of the applicability of the strongly correlated one-band model to the cuprate superconductors. Similar conclusions have been reached by Eskes & Sawatzky (1990) and by Stephan & Horsch (1990).

5. Conclusions

The structure of the CuO_2 planes with four-fold square coordinated Cu ions and two-fold coordinated O ions points directly towards the pdσ-hybridization as the source of the stabilization energy of the planar structure. In this brief review we started from the ionic limit and discussed how by treating this hybridization as the strongest perturbation term we could arrive at a one-band strongly correlated model at low energies. This model in turn makes a series of predictions which are directly tested by nuclear resonance techniques. Also recent high-energy spectroscopy experiments support this model.

The question of the relative weight of the ionic and covalent (or hybridization)

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description is an interesting and subtle one. Recently Eskes & Sawatzky (1990) examined this question in some detail and attempted a comprehensive look at all experiments which bear on the problem. It is clear that there is strong hybridization between the Cu and O orbitals in these materials (the large values of the Heisenberg coupling J alone attest to that). An intermediate description is probably the most appropriate but this will not negate the single-band model.

In spite of a tremendous amount of activity, it is still not clear whether the simplest single-band t–J model will suffice to describe the superconductivity. The most elegant solution would be to have the high-temperature superconductivity arise as a property of the fixed point of the strongly correlated quantum liquid but at present we know too little to make a definitive conclusion on this point. Empirically the superconducting transition temperature T_c seems to be a function primarily of the hole doping concentration and the interlayer coupling.

However, in a conference such as this devoted to the interplay between electronic properties and crystal structure, it is appropriate to discuss some recent experiments which point to a curious but clear influence of a subtle change of structure. Axe *et al.* (1989) and Maeno *et al.* (1990) have found that in the $La_{2-x}Ba_xCuO_4$ series there is a region of a stability of second tetragonal phase which has a dramatic effect to reduce the value of T_c. Yet this phase is only very slightly different to the orthorhombic phase. The difference occurs through the different pattern of O-octahedra tilting in the two phases. How can such a subtle change in crystal structure influence T_c dramatically? This is another puzzle to add to the list as we try to unravel the way from the crystalline structure to the bonding pattern and then to the electronic structure and finally the superconductivity of the cuprate materials.

We are grateful to very many colleagues for informative discussions on these topics, especially, P. W. Anderson, M. S. Hybertsen, M. Schlüter, H. Monien, D. Pines, P. C. Hammel, M. Takigawa, R. E. Walstedt and W. W. Warren.

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Discussion

L. J. Sham (*University of California, San Diego, U.S.A.*). Professor Rice has given a very persuasive account of how a strongly correlated electron model can explain a number of experimental observations in copper oxides, including NMR, etc. Does this also mean that the observations necessarily imply strong correlation? If so, how is one to think of the RPA calculations of Scalapino *et al.* which explain the NMR data or of the LDA calculations of the Fermi surfaces which are still quite satisfactory?

T. M. Rice. Taking the NMR case first, the RPA calculations refer mostly to the strong AF correlations which show up in the relaxation rate. I believe they may be more applicable to the case of large hole doping where there is evidence that a Landau–Fermi liquid forms when $T_c \to 0$. For smaller hole concentration, e.g. the case of $YBa_2Cu_2O_{6.6}$ which has a strongly temperature dependent, $\chi_0(T)$, there is definitely a need for a strongly correlated model to explain the spin pairing over a large region in temperature that appears in $\chi_0(T)$. RPA gives only a constant value for the uniform susceptibility, $\chi_0(T)$.

Turning to the angle-resolved photoemission experiments, in the crudest sense they measure the value of $n(k)$, the Bloch momentum expectation value when one integrates up to the Fermi energy. We know from the one-dimensional Hubbard model that $n(k)$ drops off sharply at the Luttinger value of k_F and I expect something similar will occur in two dimensions. The detailed spectral form is another matter which requires more theory but the experiments are not obviously consistent with Landau–Fermi liquid theory.

A. O. E. Animalu (*University of Nigeria, Nsukka, Nigeria*). How does Professor Rice's model explain the observation that substitution of Cu^{II} by Zn or Ni leads to lowering of T_c, more dramatically for Zn with ($3d^{10}$) configuration than for Ni with ($3d^8$) configuration?

T. M. Rice. It is important to obtain the high-T_c superconductivity to have the Cu O_2 planes as perfect as possible and to dope them as unintrusively as possible. Dopants, such as just mentioned, which substitute on Cu planar sites are strong perturbations of the planes and destroy the integrity of the planes and in this way lower T_c.

L. M. Falicov (*University of California, Berkeley, U.S.A.*). How can Professor Rice justify a treatment of individual CuO_2 layers when these are strongly charged? The stoichiometry of $Cu^{2+} + 2O^{2-}$ yields two electrons per formula unit, a strongly charged layer indeed.

T. M. Rice. Empirically there is evidence for strong anisotropy parallel and perpendicular to the CuO_2 planes. Therefore it seems that the hopping and interactions between planes are quite small and we need to start with a good understanding of a single layer. However, the interplanar interactions may still in the end determine, T_c as for example Professor Anderson has argued on empirical grounds.

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