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LETTER TO THE EDITOR

The condensate fraction in high-T_c cuprate superconductors

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Abstract. Although it is some years since the discovery of high-T_c cuprate superconductors, the nature and doping dependence of the condensate in such materials is still uncertain. There is no consensus as to whether the supercurrent is carried by a macroscopic quantum condensate of electron pairs or hole pairs. Here we show that the experimentally measured muon spin relaxation rate, which is proportional to the condensate density in high-T_c cuprate superconductors, closely follows the upper bound given by C N Yang's theorem for condensation within a single band. This is significant because Yang's well known exposition of superconductivity as off-diagonal long-range order is very widely accepted. We infer that the condensate transports negative charge in electron-doped and hole-doped cuprate layers, which rationalizes the experimental observation that the London moments of conventional superconducting metals and superconducting ceramics have the same sign. The models that reproduce this behaviour and give a short coherence length involve real-space pairing on a lattice, possibly arising from repulsive correlations or some other pairing mechanisms.

Following Yang's equation (9) [1] for a collection of $2N$ electrons energetically restricted to a set of $2M$ single-electron states, the maximum number of condensed electrons in a superconducting condensate is given by

$$2N(1-N/M)+2N/M. \tag{1}$$

Hence for practical purposes the maximum condensate fraction should not exceed $1-\rho$, where $\rho = N/M$ is the filling fraction of the usable states.

Consider a copper/oxygen layer of a high-T_c cuprate superconductor [2, 3] containing M CuO_2 clusters where each unit contributes two single-particle eigenfunctions with opposite spin to a band of states. For hole doping, a full valence band with $\rho = 1$, and for electron doping, an empty conduction band with $\rho = 0$ in the undoped materials will be important. These two bands will correlate with different molecular orbitals in the CuO_2 clusters and we note that the validity of (1) is not dependent on the precise functional form or representation of the set of $2M$ single-particle eigenfunctions. If the 'volume' of the cluster is ν_{cell} then (1) predicts that for $2N$ electrons in a single band the condensed electron density n_s can attain a maximum value of

$$n_s = 2\rho(1-\rho)/\nu_{cell} \tag{2}$$

and it is the condensate density and not the normal-state free-carrier density that should be used in penetration depth calculations. Hence, in a weak coupling BCS superconductor the penetration depth as calculated by the conventional London method gives values which are typically a factor of five too small. Non-local theories are then required to reduce the effective condensate density to about ~4% of the total electron density. Yang's theory applied to such a case gives this reduction too. Attempts are underway to quantify this statement.

Extensive studies [4,5] of muon spin relaxation in cuprate superconductors have shown that the rate of relaxation, σ, is governed predominantly by the in-plane penetration depth λ and hence reflects the screening current in the copper/oxygen planes. In general σ is proportional to λ^{-2} and therefore to $e^2 n_s \mu_0/m$ in the clean limit, and this allows n_s/m to be compared in different materials. We assume that m is the free-electron mass. Support for this assumption comes from London moment measurements [6,7] which indicate that the mass in the London equation is the free-electron mass [8] irrespective of the nature of the material and is hence independent of doping.

If the electrons in a band are maximally condensed the above arguments suggest that the muon spin relaxation rate should be proportional to $\rho(1-\rho)/\nu_{\rm cell}$. Extensive measurements of the muon spin relaxation rate have been made particularly by Uemura [4,5] and co-workers for p-type cuprates. In the well studied materials $YBa_2Cu_3O_y$ and $La_{2-x}Sr_xCuO_4$, $\nu_{\rm cell}$ = 90.5±3.5 Å^3 as indicated by crystal structure data [9,10], so we might expect that σ will be effectively proportional to $\rho(1-\rho)$ over a wide range of x and y. In the composition ranges studied by Uemura *et al* [4] ($y > 6.66$, $x > 0.08$), simple valence counting can be used to estimate ρ, using Y^{3+}, Ba^{2+}, Cu^{2+}, La^{3+}, Sr^{2+}, O^{2-} as appropriate normal formal valences and where the charge deficit is balanced by removing electrons from the valence band discussed above [9,11]. Figure 1 shows a plot of σ against $\rho(1-\rho)$, where σ is taken from the data of [4]. It appears that there is a strong linear relationship between these two sets of variables and that Yang's maximal condensation may be occurring. Least-squares fitting of the data determines the constant of proportionality to be 16.77 μs^{-1}. We note that to date the results are only for compounds with $\rho \geqslant 0.7$. It is hoped that in the future new data from compounds with smaller ρ-values, in addition to more data from the existing compounds, will provide further support for this proportionality.

The maximal condensate densities in $YBa_2Cu_3O_7$ and $La_{1.85}Sr_{0.15}CuO_4$ correspond to calculated in-plane London penetration depths of 800 Å and 1300 Å respectively. These may be compared with experimental estimates [12] of 1400 Å and 2500 Å which as noted in [12] may be too high.

The condensate transports negative charge. In the region of low doping ($\rho \to 1$) the condensed electron pair density/cell is $\rho(1-\rho)$ and this is numerically close to the corresponding hole pair density $(1-\rho)$, and it might be argued that the condensate is formed from positively charged holes paired in real space since a plot of $\sigma/(1-\rho)$ would be linear for the first eight or nine points in figure 1. Indeed, many models have been proposed that envisage the superconducting condensate as one of a bosonic pair of holes in real space each with charge $+2e$. However, we do not believe that this can be occurring on the basis of the following argument. A genuine condensate of positively charged pairs with positive mass generates a London moment of reverse sign from that of a negatively charged condensate. In a superconductor the condensate is decoupled from the material lattice. In a topologically non-trivial geometry, for example, a dissipationless condensate current can thus flow in a loop and confine an

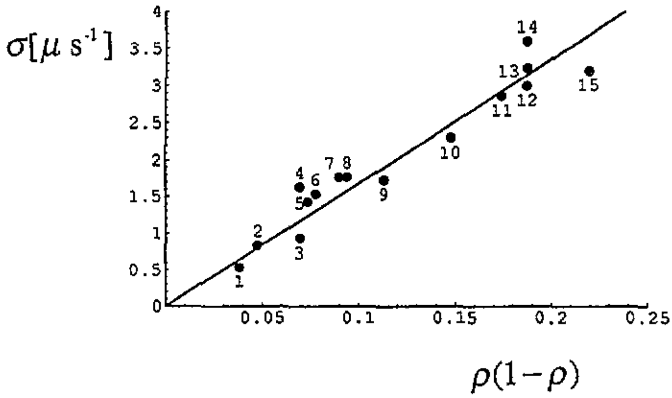

Figure 1. A plot of σ against $\rho(1-\rho)$ for $La_{2-x}Sr_xCuO_4$ and $YBaCu_3O_y$. The σ data set from [4]. The points correspond to the following values of x or y: (1) $x = 0.08$; (2) $x = 0.1$; (3) $x = 0.15$; (4) $x = 0.15$; (5) $y = 6.66$; (6) $y = 6.67$; (7) $x = 0.20$; (8) $x = 0.21$; (9) $y = 6.76$; (10) $y = 6.86$; (11) $y = 6.95$; (12) $y = 7.0$; (13) $y = 7.0$; (14) $y = 7.0$. Point 15 is for $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_7$ where we have assumed Ca^{2+} in the calculation of ρ. The straight line is the least-squares fit of the data to $A\rho(1-\rho)$ where A is a fitting constant which is determined to be 16.77 μs^{-1}.

integral multiple of magnetic flux quanta Φ_0 $(=h/2e)$. This decoupling is such that when a superconducting sample (i.e. the material lattice) is rotated with an angular velocity ω, the condensate initially remains stationary in the laboratory frame, and a magnetic field results [6–8] due to the relative motion. The initial time dependence of this field generates an electric field, so the condensate is then set in motion. The London equation $\nabla \times \boldsymbol{j}_s = -n_s e^2 \boldsymbol{B}/m$, along with the Maxwell equation $\nabla \times \boldsymbol{B} = \mu_0 \boldsymbol{j}_{tot} = \mu_0(\boldsymbol{j}_s - n_s S e \boldsymbol{\omega} \times \boldsymbol{r})$, yields the result that the effective magnetic field $(\boldsymbol{B} + 2mS\boldsymbol{\omega}/e)$ exhibits the Meissner effect. Here $\boldsymbol{j}_s$ is the superconducting current density and S is the sign of the lattice charge. Thus, apart from in the surface penetration layer where the condensate current does not balance that of the lattice, the London field inside the superconductor is

$$\boldsymbol{B} = (2mS/e)\boldsymbol{\omega}. \tag{3}$$

For conventional superconductors $\boldsymbol{B}$ is negatively proportional to ω as $S = +1$, and it is clear that for a genuine positively charged condensate this will reverse due to the sign change in S required by electroneutrality. We note, however, that the experimentally measured [6, 7] London moments of conventional metallic superconductors (e.g. Pb) and YBCO have the same sign and magnitude indicating that the condensate in hole-doped cuprates is as in conventional materials and carries negative charge.

A theoretical model where the condensate density is equal to Yang's upper bound and which also accounts for the symmetry in the superconducting, insulating and metallic phases of doped cuprates has been discussed elsewhere [13, 14] (see (27) in [13]). The simultaneous attainment of maximal condensation with a short coherence length requires a wavefunction in which all possible configurations of pairwise-occupied Wannier cells contribute with equal weight to the many-electron wavefunction. Other real-space pairing models, or variations of them, may also achieve this. For example Mott's spin bipolaron model [3, 15] may be extended to include the effects of the cuprate lattice, and the essence of other local pair models of the de Jongh [16], Alexandrov and Micnas [17] types (these latter models are reviewed in [17]) may be treated assuming an effective Hamiltonian of the form

$$\sum_i h(i) + \tfrac{1}{2} \sum_{i,j}{}' g(i,\ j)$$

using the formalism given in [13], restricting each pair to a single Wannier cell. From a density matrix viewpoint there is no true amplitude for hole condensation. However, if the pairing of holes in such models is energetically favoured this also requires the electrons on the lattice to pair and it is the paired electrons that may condense as discussed in [13]. If the superconducting state is energetically allowed, the condensate fraction is given as above and the condensate carries negative charge and positive mass. This feature is consistent with the experimental observation that the London moments of all high-T_c superconductors so far studied have the same sign and magnitude as those of conventional superconductors.

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