Two-fluid interpretation of the microwave conductivity of $YBa_2Cu_3O_{7-\delta}$

J. R. Waldram, P. Theopistou, A. Porch,* and H.-M. Cheah†
Cavendish Laboratory and IRC in Superconductivity, Madingley Road, Cambridge CB3 0HE, United Kingdom
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The use of the two-fluid model for analyzing the microwave conductivity of $YBa_2Cu_3O_{7-\delta}$ is critically appraised for *s*-wave and *d*-wave models and for weak and strong scattering, in the light of published results on single crystals, and of results here presented on high-quality epitaxial films and powders doped with Zn and Co. It is argued that the normal electrons in the best samples show nonlocal conductivity ($\lambda < \ell$ below 40 K), and that this provides a natural explanation of the low-temperature behavior of the measured surface impedance. If correct this model is firmly in favor of *d*-wave pairing. Evidence is shown that some 10% of electrons remain normal at $T=0$ in good films and 50% or more in heavily doped powders, in states which may or may not be localized. This behavior is associated with a T^2 term in the temperature dependence of λ and is in accord with recent calculations of the effects of strong scattering impurities. It is argued that in the superconducting state transport between localized states is not necessarily associated with hopping conduction, because of the effects of Andreev reflection. [S0163-1829(97)06005-0]

I. INTRODUCTION

Recent measurements by us of the surface impedance of good-quality optimized $YBa_2Cu_3O_{7-\delta}$ films have given results for the complex conductivity which, in the best films, are similar to those obtained by the University of British Columbia (UBC) group for good-quality single crystals.[1,2,11] Analysis of these results using the two-fluid model employed by the UBC group[2] and others has raised questions which we explore in this paper. In Secs. II–VI we appraise the theory of the two-fluid model and its applications to single-crystal $YBa_2Cu_3O_{7-\delta}$, including the questions of whether the normal current response of $YBa_2Cu_3O_{7-\delta}$ becomes nonlocal at low temperatures. In the remaining sections we discuss our own results for $YBa_2Cu_3O_{7-\delta}$ thin films and for doped powders, examining the question of whether the normal fraction f_n varies as T or as T^2 at low temperatures, the question of whether $f_n \to 0$ at low temperatures, and the roles of weak and strong impurity scattering.

II. THE CONVENTIONAL TWO-FLUID MODEL

In the conventional two-fluid model the complex conductivity is written as

$$\sigma = \sigma' - i\sigma'' = \frac{ne^2}{m}\left[\frac{f_s}{i\omega} + \frac{f_n}{1/\tau + i\omega}\right], \tag{1}$$

where the electron density n is divided between superconducting and normal fractions f_s and f_n, with $f_s + f_n = 1$, and τ is the normal electron relaxation time. (We reserve the notation $\sigma = \sigma_1 - i\sigma_2$ for the weak-scattering, dirty-limit conductivity of Mattis and Bardeen.[3] On the assumption that $f_n \to 0$ at $T=0$ one may use Eq. (1) to extract $\omega\tau$ and f_n from the measured conductivity as

$$\omega\tau = \frac{\sigma'(T)}{\sigma''(0) - \sigma''(T)} \tag{2}$$

and

$$f_n = (1+\omega^2\tau^2)\frac{\sigma''(0) - \sigma''(T)}{\sigma''(0)}. \tag{3}$$

The UBC group and others have used these relations[2] to obtain $\omega\tau$ and f_n from the observed microwave conductivity in the *a-b* plane of good-quality single crystals of $YBa_2Cu_3O_{7-\delta}$, with the following important results: (i) τ is independent of the frequency of measurement, as expected; (ii) τ increases rapidly by two orders of magnitude as T falls from 85 to 40 K in optimized $YBa_2Cu_3O_{7-\delta}$; (iii) τ becomes constant below 40 K in optimized $YBa_2Cu_3O_{7-\delta}$; (iv) a small amount of Zn doping reduces τ, but small variations in O doping near optimum doping have little effect on τ; (v) f_n varies linearly with T at low temperatures; and (vi) the conductivity has essentially the same *form* as a function of T for current flow in the *a* and *b* directions, but in *magnitude* is about twice as high in the *b* direction (the chain direction), for both real and imaginary parts.

III. THE TWO-FLUID MODEL FOR WEAK SCATTERING MICROSCOPIC THEORY

Superconductors may be described by a local conductivity σ when the electronic mean free path ℓ is much smaller than the penetration depth λ. For currents flowing in the *a-b* plane in $YBa_2Cu_3O_{7-\delta}$ the penetration depth λ is always greater than 140 nm, while the electronic mean-free path ℓ is less than 10 nm at T_c, though it increases with falling T. In general we might therefore expect that nonlocal effects should be unimportant. (See, however, Sec. VI.)

BCS electromagnetic response theory was originally developed by Mattis and Bardeen.[3] In optimized $YBa_2Cu_3O_{7-\delta}$ the electromagnetic coherence length ξ_0 for currents flowing in the *a-b* plane is of order 1.5 nm so we normally have ℓ considerably greater than ξ_0 (though still smaller than λ). In this *clean local limit* of Mattis-Bardeen theory the supercurrent conductivity reduces at low frequencies to the well-known BCS expression for the *London limit*

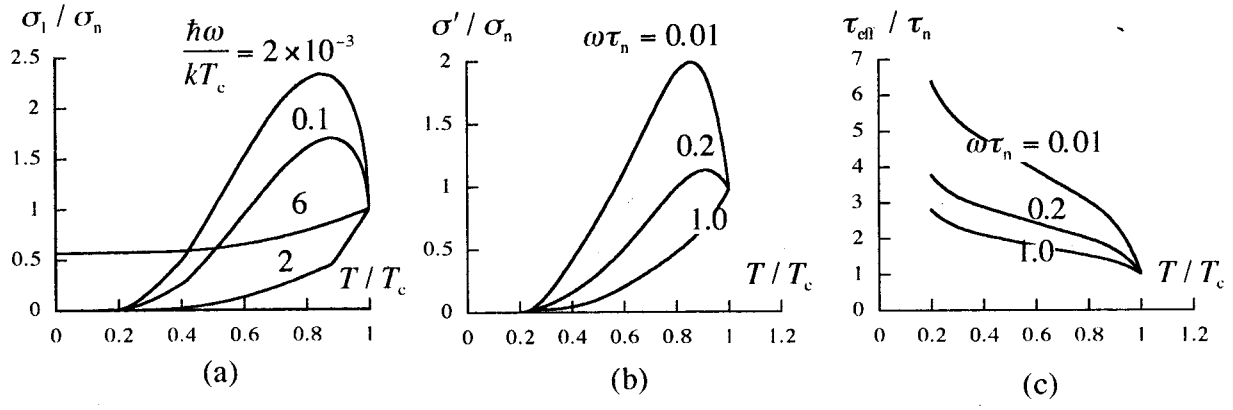

FIG. 1. Computed real part of the high-frequency conductivity for an s-wave superconductor in the weak-scattering limit when τ_n is independent of energy, normalized to the dc conductivity σ_n. (a) Mattis-Bardeen conductivity $\sigma_1(T)$ in the dirty limit $\ell \ll \xi_0$ for various values of $\hbar\omega/kT_c$, showing the well-known coherence peak. (b) The two-fluid conductivity $\sigma'(T)$ given by Eq. (7) in the clean local limit $\xi_0 \ll \ell \ll \lambda$ for various values of $\omega\tau_n$. (c) Values of $\tau_{\rm eff}/\tau_n$ corresponding to (b).

$$\frac{ne^2}{m}\frac{1}{s+i\omega}\left[1-\int_{-\infty}^{\infty}-\frac{\partial f}{\partial E}\,d\varepsilon\right], \tag{4}$$

where s is an infinitesimal, and the normal current conductivity becomes equal to

$$\frac{ne^2}{m}\int_{-\infty}^{\infty}\left(-\frac{\partial f}{\partial E}\right)\frac{1}{1/\tau_s+i\omega}\,d\varepsilon, \tag{5}$$

where τ_s is the energy-dependent relaxation time of the excitations in the superconducting state (see Appendix). On comparison with Eq. (1) we see that in the clean local limit of Mattis-Bardeen theory, the two-fluid model holds provided (i) we make the identification

$$f_n=\int_{-\infty}^{\infty}-\frac{\partial f}{\partial E}d\varepsilon \tag{6}$$

and (ii) we replace $1/(1/\tau+i\omega)$ by the appropriate weighted average over states. After allowing for this averaging we find that

$$\frac{\sigma'}{\sigma_n}=\int_{-\infty}^{\infty}(-\partial f/\partial E)\frac{\tau_s}{1+(\omega\tau_s)^2}d\varepsilon/\tau_n, \tag{7}$$

where we have normalized to the normal-state dc conductivity σ_n and τ_n is the normal-state relaxation time. If this relaxation time varies with energy, as is likely in the cuprates, it must be replaced by the effective average value

$$\tau_{n,\rm eff}=\int_{-\infty}^{\infty}(-\partial f/\partial\varepsilon)\tau_n d\varepsilon.$$

The effective value of $\omega\tau$ obtained experimentally from Eq. (2) may be identified as

$$\omega\tau_{\rm eff}=\int_{-\infty}^{\infty}(-\partial f/\partial E)\frac{\omega\tau_s}{1+(\omega\tau_s)^2}\,d\varepsilon\Big/\int_{-\infty}^{\infty}\frac{-\partial f/\partial E}{1+(\omega\tau_s)^2}d\varepsilon. \tag{8}$$

Mattis and Bardeen assumed weak coupling and weak elastic scattering describable as a first order process in a temperature-independent scattering potential (the Born limit). In this limit the local perturbation of the electron wave functions by the potential is small and τ_n is independent of energy. After allowing for the BCS density of states and coherence factors, the scattering time τ_s is found for an s-wave superconductor to be equal to $(E/\varepsilon)\tau_n$, which is strongly energy dependent and diverges at the gap edge. (The mean-free path ℓ_s, however, is independent of energy and equal to ℓ_n).

In the opposite extreme of Mattis-Bardeen theory, the *dirty limit* $\ell \ll \xi_0$, the complex conductivity is conveniently written as $\sigma_1 - i\sigma_2$, expressed in terms of the tabulated Mattis-Bardeen conductivity ratios σ_1/σ_n and σ_2/σ_n which are independent of ℓ. As is well known, the ratio σ_1/σ_n shows a *coherence peak* whose form depends on the parameter $\hbar\omega/\Delta$ [Fig. 1(a)]. It is less widely realized that, on the same assumption, a similar peak is apparent in the clean local limit expression (7), whose form, however, depends on the different parameter $\omega\tau_n$ [Fig. 1(b)]. (The peaks are both associated with the logarithmic divergence of the conductivity integral with respect to energy near $\varepsilon=0$. In the dirty limit the divergence is cutoff at the energy for which the distinction between E_1 and $E_2=E_1+\hbar\omega$ becomes important, an effect which depends on the parameter $\hbar\omega/\Delta$. In the clean local limit the cutoff occurs when $\omega\tau_s$ becomes large, a higher energy; and this effect depends on the parameter $\omega\tau_n$.) From the two-fluid point of view the clean-limit peak has a simple interpretation: it is related to the energy dependence of the scattering time τ. As T falls an increasing proportion of the excitations is near the gap edge, and this increases $\tau_{\rm eff}$, as Fig. 1(c) shows. It is this increase which leads to the peak $\sigma'(T)$ in the weak elastic scattering model.

The corresponding conductivity for a d-wave model has been computed by Hirschfeld *et al.*,[4] who showed that the two-fluid Eqs. (4) and (5) hold in that case also, if the integral over ε is interpreted as a sum over k states. In this model the gap parameter Δ is anisotropic, with nodes in k space and a maximum value Δ_0. As T falls the dominant excitations are increasingly concentrated near the nodes, and this makes f_n

of order kT/Δ_0 at low T. As T falls the typical excitation energy E and the corresponding local value of the gap parameter Δ for the dominant excitations near the nodes both fall in proportion to T. It follows that the typical coherence factors and the E/ε factor in the density of states per range of angle are independent of T at low temperatures and not very different from their normal-state values. But for elastic scattering the final state is limited to k values near a node and the fraction of angles available for the final state is of order kT/Δ_0. We therefore expect that τ_s will be of order $(\Delta_0/kT)\tau_n$, as the detailed calculations confirm. Thus we again expect τ_s to rise in comparison with τ_n as T falls, as in the s-wave model, but for a different reason. In fact, since f_n is of order kT/Δ_0, the T dependences of τ_s and f_n cancel out in the low-frequency conductivity and we are left at low T with a *constant* conductivity close to σ_n. At higher frequencies the $1+(\omega\tau_s)^2$ denominators pull the theoretical value of σ' below this value increasing as T falls (Fig. 2 of Ref. 4).

IV. EFFECTS OF STRONG SCATTERING

It is unlikely that impurities of different valence which substitute for Cu within the CuO_2 superconducting planes can be treated as weak scatters and this is confirmed by the fact that a few % of Zn impurities has a strong effect on T_c, showing that they must be producing a substantial perturbation of the electron wave functions nearby. Several authors have therefore developed theories[5] of the effects of dilute strong scatterers, usually assuming, for simplicity, the largest possible scattering corresponding to a phase shift of $\pi/2$ in the s-wave channel, with negligible scattering into other channels (isotropic scattering). The large perturbation produced by a strong scatterer has three important effects: (i) it may have a strong effect on the order parameter and hence on the transition temperature; (ii) it changes the density of states and hence the effective normal carrier concentration; and (iii) it modifies the scattering cross section, and hence τ as a function of energy.

The effects of scattering on the gap parameter Δ and density of states N_s were explored recently in numerical calculations by Xiang and Wheatley.[6] They found that weak scattering had little effect on s-wave material, in accordance with Anderson's theorem,[7] while in d-wave material it had little effect on the order parameter, but did introduce a small density of states at zero energy. For strong scattering with a large phase shift, on the other hand, Anderson's theorem does not hold when the phase shift is strongly energy dependent, and Xiang and Wheatley found that for their scattering model the order parameter was very substantially reduced in both s- and d-wave material for 7% of impurities, with a density of states at zero energy approaching the normal-state value. In d-wave material at low energies N_s is linear in E in the absence of defects, but has the form $A+BE^2$ when defects are present, as previously predicted by Gor'kov and Kalugin.[8] Using scattering parameters fitted to the normal-state resistivity, the Xiang and Wheatley model gives a good semiquantitative account, for instance, of the suppression of T_c and the electronic heat capacity observed[9] at low T in Zn-doped $YBa_2Cu_3O_{7-\delta}$.

The extra density of states at low energies induced by scattering centers has also been predicted using analytical methods. Generally speaking, for a typical relaxation time τ the extra density of states at zero energy is of order $N_F(\hbar/\Delta\tau)$, and it makes a significant extra contribution at energies up to $\hbar/\tau$. As was pointed out by Lee,[10] when we calculate the contribution of these low-energy excitations to the low-frequency conductivity, the terms in τ cancel and we are left with a small constant contribution σ_{00} of order $(ne^2/m)(\hbar/\Delta)$, which should dominate the conductivity up to a temperature T^* of order $\hbar/\tau k$. This temperature is low for materials near the clean limit, making the effect difficult to observe, but it should be possible to see it in Zn-doped $YBa_2Cu_3O_{7-\delta}$. At temperatures above T^* the extra density of states does not contribute significantly to the carrier concentration, but there is a large renormalization of the scattering rate. Hirschfeld *et al.*[4] have computed the effects of strong scattering described by a t matrix. They find, strikingly, that the renormalized scattering rate is roughly proportional to Δ_0/E, corresponding to a cross section which diverges at low energy and a conductivity proportional to T^2 for low temperatures above T^*.

V. THE COMPLEX CONDUCTIVITY OF $YBa_2Cu_3O_{7-\delta}$ BELOW 40 K

We start by assuming that $YBa_2Cu_3O_{7-\delta}$ is in the clean limit and that the two-fluid equations (4) and (5) apply. [Although these equations have been deduced for weak elastic scattering, the sum-rule argument described in the Appendix and the natural form of Eq. (5) suggest that they may hold for scattering for all types in the clean limit.]

At low temperatures σ'' falls *linearly* with T in the best single-crystal samples and since $\omega\tau$ becomes constant at low T it follows from Eq. (3) that $f_n \propto T$. The BCS expression (6) for f_n may be rewritten as

$$f_n = 2\int_0^\infty \left(-\frac{\partial f}{\partial E}\right) N_s(E)\,dE. \tag{9}$$

For an s-save superconductor this formula predicts that f_n falls exponentially at low T, but for a d-wave superconductor which has Fermi surface nodes in the energy gap the low-lying density of states is proportional to E, and it is easy to show that Eq. (9) predicts that f_n will be proportional to T, as observed. This has been taken as strong evidence for the d-wave model.[11] [If this explanation is correct, it seems to require that the chain electrons must have nodes too, for otherwise we cannot easily explain why $\lambda(T)$ has the same form for currents flowing in the a and b directions.]

As we have noted, $\tau_{\rm eff}$ rises rapidly with falling T but becomes constant below 40 K in the best single crystals of $YBa_2Cu_3O_{7-\delta}$. It has been suggested[2] that this may be understood if below 40 K the dominant scattering in the best single crystals is elastic scattering by defects. However, as Hirschfeld *et al.* have emphasized,[4] it is important to consider carefully the energy dependence of τ. As Fig. 1(c) shows, in the clean limit of Mattis-Bardeen theory the value of $\tau_{\rm eff}$ obtained from Eq. (2) for s-wave superconductors in the elastic-scattering regime is not constant, but rises appreciably at low T, even for values of $\omega\tau$ of order unity. This observation suggests strongly that we cannot be dealing with

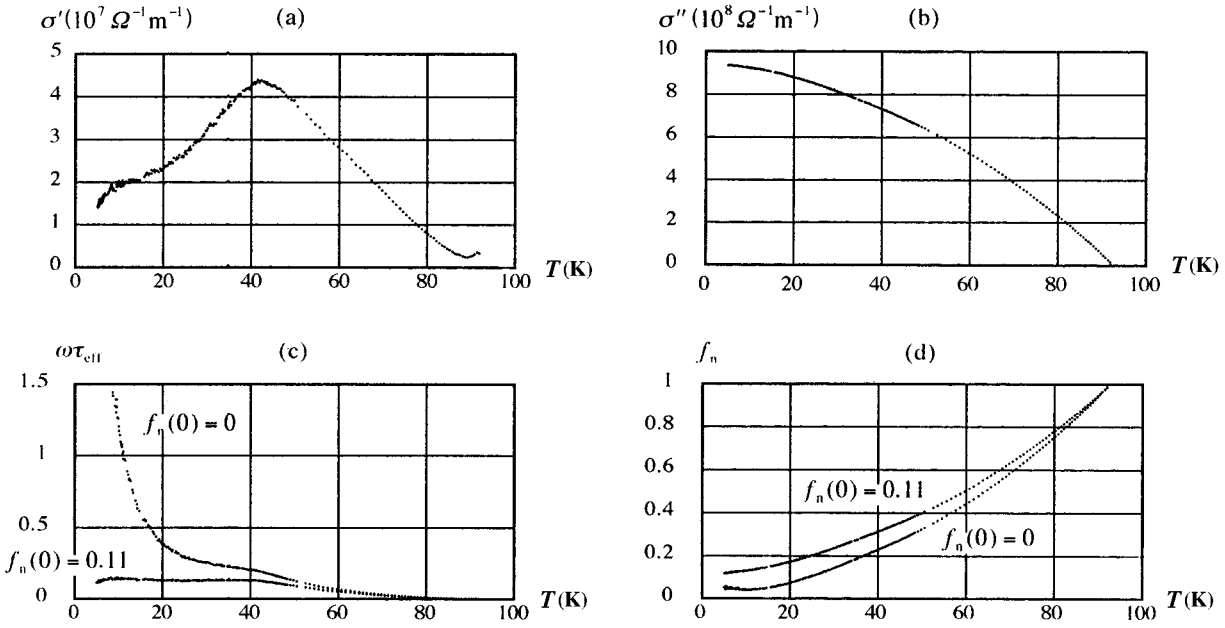

FIG. 2. Results for a high-quality epitaxial $YBa_2Cu_3O_{7-\delta}$ film from DRA Malvern. (a) and (b) Real and imaginary part of the measured microwave conductivity. (c) and (d) Corresponding values of $\omega\tau_{\rm eff}$ and f_n, for two assumed values of $f_n(0)$.

an *s*-wave superconductor whose dominant excitations move ever closer to the gap edge as T falls. But the observed behavior does not correspond to a *d*-wave model either, for which τ should vary at $1/T$ in the Born limit and as T in the more realistic strong-scattering limit (at the temperatures above T^* for which reasonably accurate measurements are possible in the best crystals).

It is, moreover, a remarkable fact that the peak observed by the UBC group in σ' in $YBa_2Cu_3O_{7-\delta}$ always appears near 40 K (unless impurities such as Zn or Co have been added) and that $\tau_{\rm eff}$ always settles at about the same level of 5×10^{-12} s. This seems to require that the supposed residual scattering always has the same strength. This is true not only for optimized material, but also when the O doping is varied, and for thin film and powder samples which appear to contain extra defects [Fig. 2(a)]. Moreover, in optimized single crystals an obvious source of defect scattering for the chain electrons is oxygen disorder on the chains, which is known to vary considerably according to the method of preparation. A similar peak has recently been found[12] in $Bi_2Sr_2CaCu_2O_{8+\delta}$.

VI. THE POSSIBILITY OF NONLOCAL CONDUCTIVITY BELOW 40 K

These considerations raise the question of whether $\tau_{\rm eff}$ might be limited not by the residual scattering but by some intrinsic property. We suggest that this is indeed so, for the following reason. A value for the Fermi velocity in the *a*-*b* plane in $YBa_2Cu_3O_{7-\delta}$ of about 1.6×10^5 ms^{-1} may be obtained from the normal-state heat capacity. [We assume that ν_F is about the same on the chains and the planes, as the band structure calculations predict, and that the perimeter of the two-dimensional (2D) Fermi surface agrees with the band structure perimeter, as the angle-resolved photoemission spectroscopy observations suggest. The value obtained corresponds to the band structure value with a modest mass renormalization.] If the velocity of the excitations remains of this order in the superconducting state, as would be expected in a *d*-wave model, we may deduce from the limiting value of $\tau_{\rm eff}$ that the limiting mean-free path must be as long as 10^{-6} m. But this is greater than the penetration depth, and we must therefore ask whether the normal electrons may have entered the anomalous skin effect regime.[13]

A simple way of viewing the anomalous skin effect is to say that the effective free path of the electrons is limited by the skin depth itself, which sets an upper limit to the distance which a typical excitation can travel while remaining in the rf electric field. The situation is complicated in $YBa_2Cu_3O_{7-\delta}$ by the fact that the Fermi surface is nearly two dimensional; as was pointed out by Chang and Scalapino,[14] for a *completely* layered material the electrons have no velocity in the *c* direction and all nonlocal effects disappear for currents flowing within the *a*-*b* plane. However, as noted by Zuccaro *et al.*,[15] the *c* component of electron velocity cannot be ignored in $YBa_2Cu_3O_{7-\delta}$. Reference to the band structure Fermi surface[16] shows that in the dominant chain and plane bands the electronic excitations are moving at not more than 20° to the *a*-*b* planes and in most cases considerably less. We may thus estimate the typical velocity in the *c* direction as about 3×10^4 ms^{-1}. (Zuccaro *et al.* used an unexplained value of 8×10^4 ms^{-1}, but suggested that it should be reduced to 2×10^4 ms^{-1} to obtain good agreement with early microwave data and with the observed anisotropy of B_{c2}.) If these values are to be believed the effective limit to the *a*-*b* plane free path set by nonlocal behavior for typical electrons will be about 5 times λ. This is close to our estimate of the limiting value actually observed and suggests strongly that in the purer samples the limit to $\tau_{\rm eff}$ is set by the sample's reaching the nonlocal regime rather than its reaching a residual resistance limit.

Unlike the residual scattering picture, such a description

seems to explain the observed behavior of τ_{eff} at low T, but only if we adopt a d-wave model. For a d-wave model the velocity of the dominant excitations remains constant as T falls and not very different from ν_F. This makes a constant effective mean-free path limited by λ correspond to a constant τ_{eff}, as observed in the best single crystals. (It also makes our estimate of the anomalous limit cutoff self-consistent.) For an s-wave model, on the other hand, the velocity of the dominant excitations would fall as T falls, making a constant effective mean-free path correspond to an increasing τ_{eff}, contrary to observation.

VII. OBSERVATIONS ON THIN FILMS

We have measured the bandwidth and resonant frequency, at about 6 GHz, of a parallel plate half-wave resonator, of which the samples, thin films deposited on an MgO substrate, formed one half. The resonator was calibrated by making equivalent observations on chemically polished normal metal samples, whose surface impedance could be computed from the theory of the anomalous skin effect. Frequency corrections for thermal expansion were applied, using an algorithm whose validity was successfully checked for the normal metal calibrators. The real and imaginary parts of the surface impedance were measured on the same samples, in the same experiment. Full details will be published elsewhere.[17]

The best films appeared to have few extended defects such as grain boundaries. We therefore assumed for them that the observations could be accounted for a uniform complex conductivity, which we obtained from the measured surface impedance after allowing for the finite thickness of the film. Figures 2(a) and 2(b) show as an example the conductivities for an optimized $YBa_2Cu_3O_{7-\delta}$ film prepared at DRA Malvern by coevaporation, and supplied to us by Professor R. G. Humphreys. This film was 340-nm thick and was grown on a homoepitaxially buffered MgO substrate at 690 °C under a pressure of 2×10^{-4} mbar of oxygen, up to 50% of which was atomic and subsequently cooled in an oxygen pressure of 2×10^{-2} mbar with a smaller atomic fraction. After growth it was furnace annealed for 30 min at 500 °C in 1 bar of oxygen. It was accurately c oriented: the rocking curve for the (005) reflection had a width of 0.35°. The atomic force microscope scan showed a smooth surface with undulations on a scale of about 50 nm. The resistivity at 100 K was 81 $\mu\Omega$ cm, and the critical current density was 3.2×10^6 Acm^{-2}.

The conductivities obtained are broadly similar in form to those obtained on single-crystal $YBa_2Cu_3O_{7-\delta}$ by the UBC group, though the real part of the conductivity is a little larger. There is, however, an important difference. At the lowest temperature σ'' varies *quadratically* with T, while in the single crystals it varied *linearly*. This quadratic behavior of σ'' has a dramatic effect when we calculate $\omega\tau_{\text{eff}}$ using Eq. (2). At high temperatures $\omega\tau_{\text{eff}}$ increases with falling T and flattens off at 40 K, much as in the UBC results; but below 30 K it starts to rise, and seems to be *diverging* at low T [Fig. 2(c)]. When we calculate f_n using Eq. (3) we find an *upturn* below 10 K [Fig. 2(d)].

TABLE I. Characteristics of heavily doped $YBa_2Cu_3O_{7-\delta}$ powders. Labels show the proportion of Cu atoms replaced by the dopant.

	1.5% Co	4% Co	5% Zn	Undoped
T_c/K	90	80	39	93
$f_n(0)$, from heat capacity	<0.9	<0.7	0.8	0
from λ_{ab}	0.5	0.5	0.8	0
λ_{ab}/nm, from ac susceptibility	190	190	310	135

VIII. INTERPRETATION OF THE THIN FILM RESULTS

The two-fluid interpretation used so far leads to results for our films which seem nonphysical: the rapid rise in $\omega\tau_{\text{eff}}$ below 30 K and the upturn in f_n below 10 K seem intrinsically implausible, especially when compared with the single-crystal results. Moreover, the values of τ correspond to a mean-free path much greater than λ, which should be unobservable as discussed in Sec. VI.

We note, however, that Eqs. (2) and (3) both depend on the assumption that $f_n\rightarrow0$ as $T\rightarrow0$. It is easy to relax this assumption: both equations remain valid provided we replace $\sigma''(0)$ by σ_0'', the larger value which σ'' *would* have taken if all the electrons had become superconducting. Figures 2(c) and 2(d) show the effect of adopting a plausible trial value for σ_0''. We note that, if we choose a value for σ_0'' which makes some 11% of the electrons remain normal at $T=0$ for this sample, the above difficulties disappear: we obtain values of $\omega\tau_{\text{eff}}$ which vary with temperature essentially as observed in the single-crystal work and f_n decreases monotonically with falling T. This behavior of f_n is similar to that shown in Fig. 11 of Ref. 4, which was deduced by fitting $\lambda(T)$ for imperfect single crystals, which had a quadratic form at low T, as is commonly observed in all but the best samples.

This model is supported by the calculations of Gor'kov and Kalugin[8] and of Xiang and Wheatley[6] which showed that the excitation density of states $N_s(E)$ present when point defects are introduced into a d-wave superconductor has the form $A+BE^2$. If we once again use Eq. (9) we find that f_n should be proportional to $A'+B'(kT)^2$ in the presence of defects, in accordance with the modified plot in Fig. 2(d).

IX. OBSERVATIONS ON DOPED POWDERS

Measurements which we made some years ago[18] of the complex microwave susceptibility of $YBa_2Cu_3O_{7-\delta}$ powders heavily doped with Co and Zn throw further light on the role of impurities and the question of what limits τ_{eff} at low temperatures. In these samples there was strong evidence that a large fraction of the electrons remained normal at $T=0$. Measurements of the electronic heat capacity[19] made an estimate of $f_n(0)$ possible. (See Table I: in the case of Co doping the presence of a weak magnetic anomaly below 40 K meant that only an upper limit on f_n could be obtained.) Measurements of the ac susceptibility[20] showed that, although the form of the penetration depth as a function of T was similar to that frequently obtained in undoped $YBa_2Cu_3O_{7-\delta}$, with $\lambda(T)-\lambda(0)$ accurately proportional to T^2 at low T, the absolute value of $\lambda(0)$, which is proportional

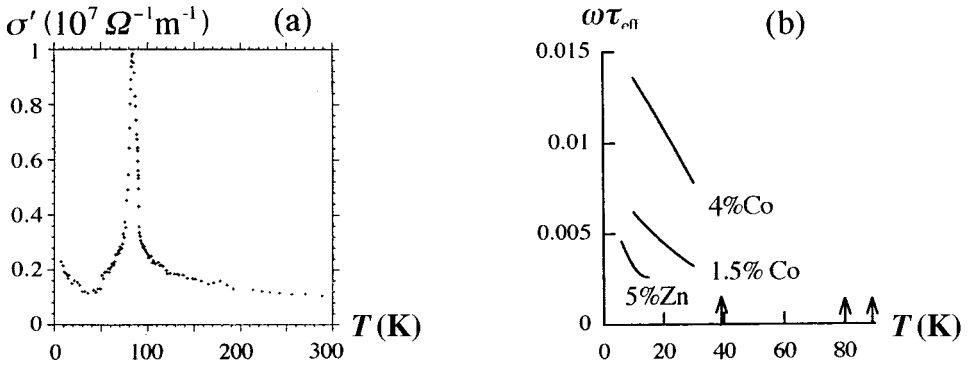

FIG. 3. Results from the microwave susceptibility of doped $YBa_2Cu_3O_{7-\delta}$ powders. (a) Real part of conductivity when 1.5% of Cu is replaced by Co. The behavior above T_c agrees with the measured dc conductivity of similar samples, including the fluctuation conductivity, and the peak is interpreted as a fluctuation peak. (b) Corresponding values of $\omega\tau_{\rm eff}$ deduced as described in the text for three doped samples, using the values of $f_n(0)$ quoted in Table I; the arrows show the critical temperatures. The analysis used here ignores fluctuation effects: values of $\omega\tau_{\rm eff}$ for $T>0.5T_c$ are therefore invalid and are omitted from the plot.

to $n_s(0)^{-1/2}$, increased substantially with doping. Since the normal-state heat capacity showed the *total* electron density had not changed with doping this made possible a second and independent estimate of $f_n(0)$.

If the shapes and grain-size distribution for the powder are known one may deduce the complex conductivity from the microwave susceptibility,[21] but in these early measurements calibration difficulties associated with the presence of a few abnormally large grains led to underestimates of the microwave conductivities by factors which varied from 2 to 7, and our results were therefore not published in full. Three qualitative conclusions were, however, apparent from the results for $\sigma'(T)$: in these heavily doped powders (i) σ'_{ab} is about one order of magnitude smaller than in the UBC single crystals at 40 K and not very different from the normal-state conductivity extrapolated below T_c; (ii) $\sigma'(T)$ continues to rise steeply at the lowest temperature reached, the peak in $\sigma'(T)$ at 40 K seen by the UBC group in optimized $YBa_2Cu_3O_{7-\delta}$ being absent [Fig. 3(a)]; and (iii) the fluctuation peak near T_c is much more noticeable and somewhat broader and appears to affect $\sigma'(T)$ down to about $0.5T_c$. Since Eq. (2) depends only on a ratio of conductivities, our calibration errors largely cancel out when the effective value of $\omega\tau_{\rm eff}$ is computed. With the help of the values of f_n from the table and our observations of $\sigma''(T)$ we deduce the effective values of $\omega\tau_{\rm eff}$ shown in Fig. 3(b), which remain imprecise but should be reasonably reliable in form and approximate magnitude.

Three general conclusions may be drawn. First, doping with both Co and Zn appears to increase dramatically the proportion of electrons remaining normal at low temperatures (and we have no evidence in these heavily doped powders of any serious discrepancy between the values of f_n determined from the heat capacity and the penetration depth measurements). Second, the relaxation time at $T=0$ is substantially decreased, as would be expected for an increased density of scattering centers. Third, τ is not constant at low T but continues to rise steadily. In interpreting this effect in such heavily doped material in which $f_n(0)$ is 0.5 or more, it seems best to suppose that the normal electrons behave much as they do in the normal state, with a constant residual scattering rate and an inelastic electron-electron scattering rate much larger than in undoped crystals, which is responsible for the temperature dependence (the effects of the condensation on the relaxation times being largely suppressed).

X. LOCALIZED STATES

Whether the new low-lying states induced by strong scattering centers are localized near the impurities or more extended is not completely clear. The numerical calculations of Xiang and Wheatley[6] suggest an intermediate case, with perturbations extending through 10 or 20 lattice spacings, but substantial changes in the gap parameter more sharply localized. The two-fluid model and the calculations of Hirschfeld *et al.*[4] ignore the possibility of confinement. Lee[10] has argued that the low-lying states will be confined and that conduction at low temperatures will be by hopping between such localized states; he argues that thermally activated hopping would give an exponential behavior hard to distinguish from that due to a finite energy gap. But Balatsky and Salkola[22] have shown that if the nature of long-range hopping in the directions of the gap nodes is taken properly into account the low-lying states will not be localized in a d-wave superconductor. In the case of the powders heavily doped with Zn one might expect statistical fluctuations in the Zn concentration to lead to variations in $\Delta(r)$ on the scale of perhaps 10 nm, which would have the effect of confining some excitations. A similar effect will occur near T_c, where spatial fluctuations in $\Delta(r)$ become important.

It seems likely that at least some situations arise in the cuprates in which excitations are localized. We wish to raise the question of whether in such a situation a model of hopping between localized states is necessarily required to understand the transport properties. The theory of normal-superconducting (NS) interfaces for s-wave superconductors[23] suggests that when low-lying excitations are confined within N regions by local variations of $\Delta(r)$, current can flow smoothly across such interfaces, normal current being converted into supercurrent by Andreev reflection and other processes with only a small boundary resistance, even for sharply localized excitations. When the variation of the one-electron potential with position near the interface is also important the boundary resistance is greater, but Andreev reflection does not disappear completely and

conversion of normal current to supercurrent can still occur. If such a picture is valid for an inhomogeneous cuprate we should be able to discuss transport properties using some form of effective medium theory rather than a hopping theory. When there are disconnected ''normal'' regions of low conductivity inside a connected superconducting matrix effective medium theory shows that the two parts behave roughly as though in parallel and one obtains results not very different from the two-fluid model, which has parallel conduction by normal and superconducting carriers. In such a picture the values for $\tau_{\rm eff}$ and f_n obtained from experiment using the two-fluid model would not be changed by large factors if one adopted a model of localized excitations. It seems to us important to discuss whether such a model is generally valid for cuprates with localized excitations of different types and we encourage theoreticians to investigate this question.

XI. CONCLUSIONS

We believe that when the excitations are not localized the two-fluid model may be applied to both optimized and doped $YBa_2Cu_3O_{7-\delta}$ over most of the temperature range, in which we have $\ell \ll \lambda$ (the local limit) and $\ell \gg \xi_0$ (the clean limit, which holds reasonably well even for doped samples), if proper allowance is made for the energy dependence of τ. We suggest that localization may not lead to qualitatively different behavior if current carried by localized excitations can be converted to supercurrent at the localization boundary.

An important exception to this conclusion arises for optimized or lightly doped $YBa_2Cu_3O_{7-\delta}$ below 40 K, where our estimates suggest that the normal electrons enter the anomalous skin-effect regime. If our analysis of this situation proves to be correct it would provide some evidence that the velocity of the dominant excitations correspond at least approximately to the band structure, Fermi-liquid model (rather than, for instance, a bipolaron or holon model). It would also provide firm evidence in favor of a *d*-wave rather than an *s*-wave model and suggests a possible resolution of the apparent disagreement with all models of impurity scattering in the local limit, noted by Hirschfeld *et al.*[4]

Samples which have deliberately been heavily doped with Zn or Co contain a large fraction of normal electrons at $T=0$, but it is not clear whether these electrons are in extended or in localized states. It seems that even good quality thin films may contain 10% of normal electrons at $T=0$, and that this is associated with a density of states of the form $A+BE^2$ at low energies which leads to the commonly observed quadratic behavior of $\lambda(T)$ at low T. This agrees qualitatively with the calculations by Hsiang and Wheatley[6] of the density of states for a *d*-wave superconductor containing impurities.

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APPENDIX: THE TWO-FLUID MODEL IN MATTIS-BARDEEN THEORY

We show here how the two-fluid model may be obtained in a simple way from the nonlocal electromagnetic kernel used by Mattis and Bardeen.[3] This kernel $I(\omega,R,T)e^{-R/\ell}$ describes how the current induced by a field at frequency ω at a given point spreads out to affect other points at distance R. In the normal state I takes the form $-i\pi\omega e^{-i\omega R/v_F}$. The supercurrent part of the kernel is associated with virtual transitions, is loss-free and is purely real. The normal current part is associated with real transitions induced by the electromagnetic field and the corresponding responses travel out from the point where the field acts with a phase factor of the form $e^{-i\omega R/v}$, where v is the velocity of the response. Using these ideas we may, at frequencies below the gap frequency, identify the normal part of I as

$$I_n(\omega,R,T)=-\pi i\int_\Delta^\infty [f(E_1)-f(E_2)] \times[(g-1)e^{-iR(\varepsilon_1+\varepsilon_2)/\hbar v_F} +(g+1)e^{-iR(\varepsilon_2-\varepsilon_1)/\hbar v_F}]dE_1, \quad \text{(A1)}$$

where $E_2=E_1+\hbar\omega$, $E^2=\varepsilon^2+\Delta^2$, f is the Fermi function, and g, which involves the electromagnetic coherence factor, is $(E_1E_2+\Delta^2)/\varepsilon_1\varepsilon_2$. The term in $g-1$ is associated with electromagnetic transitions between the electronlike and holelike branches. It has a short-range of order ξ_0 and is absent in the normal state. The term in $g+1$ is associated with electron-electron and hole-hole scattering and has long range. At low frequencies it corresponds to a disturbance traveling at the group velocity $v_s=(\varepsilon/E)v_F$ of the excitations. On subtracting the terms identified as I_n we are left with a purely real contribution I_s representing the supercurrent, which is even in ω and reduces at zero frequency to the BCS supercurrent kernel $J(R,T)$.

In the *dirty limit* $\ell \ll \xi_0$, the effective conductivity $\sigma_1-i\sigma_2$ is proportional to $I(\omega,0,T)$. The corresponding *Mattis-Bardeen conductivity ratios* σ_1/σ_n and σ_2/σ_n are independent of ℓ. Both terms in Eq. (A1) contribute to σ_1/σ_n. The two-fluid model is invalid in the dirty limit. For instance, if we introduce more scattering centers σ_2 falls, corresponding in two-fluid terms to a reduction in the density of superelectrons, but there is no corresponding increase in the density of normal electrons; in Mattis-Bardeen theory τ scales in the same way with scattering in the normal and superconducting states and we interpret the constancy of σ_1/σ_n with increased scattering as reflecting a *constant* density of normal electrons. This failure to match the two-fluid model in the dirty limit is related to a sum-rule argument. If the conductivity has the two-fluid form (1) at all frequencies it follows from the conductivity sum rule

$$\int_{-\infty}^{\infty} \sigma'(\omega)\, d\omega = \pi \frac{ne^2}{m} \tag{A2}$$

that $f_s + f_n$ must be equal to unity. In theories involving an energy gap, any two-fluid model which may hold at low frequencies will break down when the frequency reaches the gap frequency, for there is then a sudden rise in absorption. However, the real part of the conductivity in any case falls rapidly beyond the cutoff frequency $1/\tau$. If this cutoff occurs above the gap frequency, as it does in the dirty limit, then the rise in σ' beyond the gap frequency will make a substantial contribution to the sum-rule integral, and it is not possible to have a two-fluid form valid at low frequencies with $f_s + f_n$ close to unity.

In the opposite case, the *clean limit* $\ell \gg \xi_0$ for which $1/\tau \ll \Delta/\hbar$, a two-fluid model is possible. The conductivity is now proportional to $\int I_n(\omega, R, T) e^{-R/\ell} dR$. Because of its short range the first term in Eq. (A1) now makes a negligible contribution to σ. For frequencies much less than the gap frequency the contribution to I from the second term reduces to

$$I_n(\omega, R, T) = -\pi i \int_{\Delta}^{\infty} \left(-\frac{\partial f}{\partial E} \hbar\omega \right) \frac{2E^2}{\varepsilon^2} e^{-i\omega R/v_s} dE, \tag{A3}$$

where we have written $\varepsilon_2 - \varepsilon_1$ as $(E/\varepsilon)\hbar\omega$. On performing the integral over R and comparing with the normal state result one finds that the normal part of the conductivity may be written in the two-fluid form (5).

*Present address: School of Electronic and Electrical Engineering, University of Birmingham, Birmingham B15 2TT, UK.

†Present address: Physics Division, School of Science, NIE 469, Singapore 259756.

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