Microwave properties of \((\text{Pr}_x\text{Y}_{1-x})\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}\) : Influence of magnetic scattering

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We report measurements of the surface impedance \(Z = R_e + iX_e\) of \((\text{Pr}_x\text{Y}_{1-x})\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}\), \((x = 0, 0.15, 0.23, 0.3, 0.4, 0.5)\). Increasing Pr concentration leads to some striking results not observed in samples doped by non-magnetic constituents. The three principal features of the \(R_e(T)\) data - multiple structure in the transition, a high residual resistance and, at high Pr concentrations, an upturn of the low \(T\) data, are all characteristic of the influence of magnetic scattering on superconductivity, and appear to be common to materials where magnetism and superconductivity coexist. The low \(T\) behavior of \(\lambda(T)\) appears to change from \(T\) to \(T^4\) at large Pr doping, unlike that reported for Ni and Zn substitutions, and is further evidence of the influence of magnetic pairbreaking of the Pr.

Keywords: microwave absorption, penetration depth, pair breaking

In the 123 class of cuprates where \(Y\) is replaced by lanthanide elements such as La, Ce, Pr, Nd, Gd, Dy, etc., the compound \(\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}\) is insulating while all the other members of the family show a superconducting transition in the vicinity of 90K. Superconductivity in \((\text{Pr}_x\text{Y}_{1-x})\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}\) is suppressed rapidly as the Pr content is increased and the system undergoes a transition to an insulating state at \(x \sim 0.55-0.6\). Since superconductivity in the cuprates is mainly associated with the Cu-O planes, the exact role of Pr (which substitutes for \(Y\) in the 123 structure) in the \(T_c\) suppression is of fundamental interest. This also makes the Pr doped system distinct from the other transition metal doped 123 compounds where dopants like Ni, Zn, Fe are substituted at the Cu sites and thus directly affect the superconductivity in the planes. Two mechanisms for the decrease of \(T_c\) with Pr concentration have been proposed: (1) annihilation of mobile holes in the \(\text{CuO}_2\) planes by the Pr ions (hole depletion mechanism), and (2) superconducting electron pair breaking (pair breaking mechanism). Superconducting electron pair breaking could be produced by potential scattering of mobile holes by the Pr ions if \(Y\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}\) is a \(d\)-wave superconductor and by spin-dependent exchange scattering of the mobile holes by the Pr ions, which carry well-defined magnetic moments, if \(Y\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}\) is an \(s\)-or \(d\)-wave (spin-singlet) superconductor. Both of these mechanisms have been incorporated into a phenomenological model which provides a semiquantitative description of the striking variations of \(T_c\) with \(x\) and \(y\) in the \(\text{Cu}_x\text{Pr}_{y}\text{Y}_{1-x-y}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}\) system for \(0 \leq x, y \leq 0.2\) (here, mobile holes are generated by Ca and annihilated by Pr) and the pressure dependence of \(T_c\) in the \((\text{Pr}_x\text{Y}_{1-x})\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}\) system for \(0 \leq x \leq 0.5\). The hole-depletion and pair breaking mechanisms are assumed to originate in the hybridization of the localized Pr4f states and the \(\text{CuO}_2\) valence band states. The existence of Pr4f – \(\text{CuO}_2\) valence band hybridization was first proposed on experimental grounds to account for the anomalous pressure dependence of \(T_c\) of \((\text{Pr}_x\text{Y}_{1-x})\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}\) system, in analogy with the anomalous behavior of \(T_c\) under pressure in superconductors containing Ce impurities such as \(\text{La}_{1-x}\text{Ce}_x\text{CuO}_2\). To the extent that pair breaking is responsible for the depression of \(T_c\) in the \((\text{Pr}_x\text{Y}_{1-x})\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}\) system, it would be necessary to invoke Pr4f – \(\text{CuO}_2\) valence band hybridization in order to generate a sufficiently strong coupling of the Pr ions to the mobile holes in the \(\text{CuO}_2\) planes. Except for \(Ce\), the other lanthanide (Ln) ions with partially-filled 4f electron shells do not depress the \(T_c\) of \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) by a measurable amount; evidently, the Ln 4f – \(\text{CuO}_2\) valence band hybridization and, in turn, the exchange coupling of the Ln ions to the holes in the \(\text{CuO}_2\) planes is small. It is interesting to note that such a hybridization-induced exchange interaction is antiferromagnetic and should produce a Kondo effect, resulting in a depression of \(T_c\) with impurity concentration (here, Pr) that deviates from the prediction of the theory of Abrikosov and Gorkov (AG) in a manner that depends on the ratio of the Kondo temperature \(T_K\) to the \(T_c\) of the host superconductor (in this case, YBCO). Measurements of the low temperature specific heat in the range \(0 < x < 0.5\) reveal a broad anomaly in the specific heat which can be described by the sum of a term of the form \(C_s(T) = \gamma T\) with an enormous “heavy-fermion-like” value of \(\gamma\) of \(\sim 240\text{mJ/molPr} - K^2\) and a contribution \(C_M(T)\) that has been described by a spin 1/2 Kondo anomaly with a value of \(T_K\) that increases with \(x\) or an anomaly associated with antiferromagnetic ordering of the Pr ions. It has been shown that the detailed \(T_c\) vs \(x\) curve of the \((\text{Pr}_x\text{Y}_{1-x})\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}\) system does not conform to the AG theory, but can be described by the aforementioned phenomenological model.
based on both hole depletion and pair breaking in the range $0 \leq x < 0.2$. Many experiments have indicated $Pr$ to be predominantly in a $3^+$ valence state, although a mixed valence state cannot be ruled out.

There are several anomalies observed in transport and magnetization experiments which indicate that $Pr_2Y_{1-x}Ba_2Cu_3O_{7-\delta}$ has a ground state with unusual electronic properties, and which has been proposed theoretically to account for the insulating nature of $PrBa_2Cu_3O_{7-\delta}$. Neutron scattering experiments indicate long range AFM ordering of the $Pr$ moments in the insulating compound $PrBa_2Cu_3O_{7-\delta}$ with an unusually high Néel temperature $T_N$ of 17K. Overall the $Pr_2Y_{1-x}Ba_2Cu_3O_{7-\delta}$ system represents the ideal candidate to explore the effects of pair-breaking and magnetic scattering in the superconducting state.

Microwave experiments have been shown to be unique probes of the superconducting state. Measurements of the $T$ dependence of the microwave surface impedance $Z_s$ and penetration depth $\lambda$ can reveal important information regarding the gap parameter and the quasiparticle density of states. The linear behavior of $\lambda$ at low $T$ observed in YBCO and BSCCO is consistent with nodes in the in-plane gap. It is of interest to examine the role of impurities in this context, since the influence of impurities are expected to be strikingly different for a d-wave superconductor compared to the conventional s-wave type as discussed above.

In this paper, we report on complex surface impedance $(Z_s = R_s + iX_s)$ measurements on a series of $Pr_2Y_{1-x}Ba_2Cu_3O_{7-\delta}$ single crystals with $x$ ranging from 0 to 0.5. Our experiments reveal novel structure in the superconducting transition region not seen in $dc$ or low frequency probes of resistivity and magnetization. In the following sections we present the surface resistance $R_s(T)$ and the low temperature penetration depth $\lambda(T)$ data and discuss our results in terms of enhanced magnetic scattering.

I. EXPERIMENT

The single crystals were grown using a flux-growth method described in an earlier publication [1]. The $Pr$ concentration $x$ of the single crystals was inferred from their measured $T_c$'s and the $T_c$ vs $x$ curve of polycrystalline $Pr_2Y_{1-x}Ba_2Cu_3O_{7-\delta}$ samples reported in ref. [1]. Typical crystals used in our experiments were of size 0.7 x 0.7 x 0.05 mm$^3$. Surface impedance measurements were done in a superconducting Nb cavity resonator operating at a frequency of 10 GHz. The samples were mounted on a sapphire rod and a "hot finger" technique was employed to monitor the temperature dependence of the complex surface impedance from 4K to 300K. This cavity perturbation method has been extensively validated in precision measurements of $R_s$ and $X_s$ in single crystals of cuprate and borocarbide superconductors [7]. The Nb cavity is maintained either at 4.2K or below 2K and the typical background $Q_b$ of the cavity can be as high as $10^8$. The surface resistance $R_s(T)$ is measured from the temperature dependent $Q$ using $R_s(T) = \Gamma Q^{-1}(T) - Q_b^{-1}(T)$ and the penetration depth using $\Delta \lambda(T) = \sqrt{\Delta f(T) - f_b(T)}$ where the geometric factors are determined by the cavity mode, crystal size and location within the cavity. In the present setup, all measurements were done in the $TE_{011}$ mode with the sample at the midpoint of the cavity axis where the microwave magnetic fields have a maximum and the microwave electric fields are zero. In all cases, the samples were oriented with $H || c$ and currents only flow in the $ab$-plane.

II. RESULTS AND DISCUSSION

In Fig. 1, the surface resistance $R_s(T)$ for $Pr_2Y_{1-x}Ba_2Cu_3O_{7-\delta}$ with $x = 0.0, 0.15, 0.23, 0.3, 0.4, 0.5$ are shown. The data are normalized at $R_s(100K)$ to highlight the systematic variation of the surface resistance with increasing $Pr$ concentration. The normal state $R_s(100K)$ values range from 0.2 to 0.8 $\Omega$ as $x \rightarrow 0$ to 0.5. The overall temperature dependence of the surface impedance in the normal state is consistent with the expected skin depth limited response given by $R_s = \sqrt{\omega \mu \rho_n/2}$ where $\rho_n$ is the normal state $dc$ electrical resistivity. This is also well represented in the upturn in $R_s$ clearly seen for the $x = 0.5$ sample before the superconducting transition occurs. At $x = 0.5$, the $Pr$-doped system is on the verge of a metal-insulator transition and $dc$ electrical resistivity measurements indicate that this transition occurs for $x \sim 0.55 - 0.6$. This transition from a linear normal state resistivity in the metallic case to a Mott Variable Range Hopping (VRH) type behavior in the insulating regime is mirrored in the surface resistance data of Fig. 1. In particular the change in sign of $dR_s/dT$ from positive to negative just above the superconducting transition is evident as $x$ increases from 0.4 to 0.5. The transition is sharpest for the undoped YBCO sample with a width $\Delta T_c$ which increases rapidly with $Pr$ substitution. Random substitution of $Y$ atoms by $Pr$ which increases the disorder in the system combined with the magnetic scattering due to free $Pr$ ions is the likely cause for the broad transition.

An interesting feature of the data of Fig. 1 is the remarkable fine structure seen in the transition region. This is particularly accentuated in the $R_s$ data for $x = 0.23$ and $x = 0.3$ (marked by arrows). A distinct change in slope at a characteristic temperature close to midpoint of the transition width occurs and is reproducible in several $Pr$-doped crystals investigated. It is to be noted that for the same concentrations, the $dc$ resistivity and susceptibility measurements do not show any signature of
multiple features in the transition. We propose that this
Two-slope structure is a consequence of a discontinuous
change in quasiparticle scattering in the superconducting
state at characteristic temperatures. This is seen clearly
in our high frequency experiments as we probe both the
normal and superfluid response in the superconducting
state.

The residual surface resistance at low temperatures
shows an increasing trend with Pr doping, and there is
an almost an order of magnitude jump between x = 0.4 and
0.5. The most striking aspect of the x = 0.5 sample is
the upturn in Rs for T ≤ 18K and the temperature de-
pendence almost mimics the normal state data just above
the superconducting transition. This is an important ob-
servation which we believe for the first time qualitatively
captures the competing effects of magnetism and super-
conductivity in cuprates as revealed in surface impedance
measurements. It should also be pointed out that the
presence of exchange interactions due to the Pr4f mo-
moments could also result in enhanced electron-electron in-
teraction effects. In this case, many body corrections to
the low temperature quasiparticle conductivity have to
be taken into account and this can lead to the upturn in
the Rs(T) seen for higher Pr doping.

It is to be pointed out that all the anomalous charac-
teristics seen here for the PrxY1−xBa2Cu3O7−δ system
have been observed by us in our microwave experiments
of borocarbide class of magnetic superconductors [13]. In
general, a high residual surface resistance, multiple struc-
ture in the transition and the low temperature upturn in
Rs all seem to be standard electrodynamic characteristics
of systems exhibiting co-existence of magnetism and su-
perconductivity. Systematic high frequency experiments
on known magnetic superconductors would help further
understand the implication of these features.

The normalized surface reactance Xs(T) is shown in
Fig.2. The overall trend is similar to the correspond-
ing Rs(T) data with some differences particularly for the
x = 0.5 sample. Two peaks are present in the vicinity of
the superconducting transition and a third feature at
least 15K higher in temperature. It is not clear whether
these features are related to coherence effects. The sur-
face reactance also shows an upturn at low temperature
but the onset of this is about 10K lower than the corre-
sponding onset in Rs. The change in reactance is directly
related to the change in penetration depth via the rela-
tion Xs = μ0ωλ. In Fig.3, the low temperature penetra-
tion depth extracted from the surface reactance is plotted
as a function of reduced temperature (T/Tc). Measure-
ment of the absolute value of the penetration depth is not
possible with the cavity perturbation technique. How-
ever, an estimate can be obtained by setting Rs = Xs
in the normal state assuming local electrodynamics. An
estimated London penetration depth are added to each
set of data in Fig.3.

For the undoped YBCO sample (x = 0), the penetra-
tion depth is linear in temperature. This linear depen-
dence seen both in YBCO and BSCCO class of cuprates
has been considered as evidence for an order parameter
symmetry having nodes in the gap [13,14]. With Pr dop-
ing, the temperature dependence of λ changes to a power
law behavior. For the x = 0.15 and 0.4, the best fit to
the data is obtained with a T4 term. It is important to
note that the data do not show a T2 behavior reported
in thin films of YBCO [15] and Zn-doped YBCO single
crystals [16]. The change over from T to T2 dependence
in Zn and Ni doped YBCO has been interpreted as due
to a crossover from a pure d-wave state to a gapless
superconducting state. There are also a number of differ-
ences in Rs between the (Zn, Ni) and Pr doped YBCO.
In the case of Zn or Ni doped samples, although the normal
state Rs increases with doping, there is negligi-
ble change in the low temperature residual surface resis-
tance. On the contrary, the normal state and residual Rs
increase with Pr concentration in PrxY1−xBa2Cu3O7−δ.
No multiple structure is seen in the transition for Zn or
Ni doped samples. Thus there is every indication that
enhanced scattering presumably of magnetic origin plays
a major role in the surface impedance characteristics of
Pr doped YBCO.

In a recent paper, it has been theoretically proposed
that in layered superconductors it is possible to have a
novel phase transition governed entirely by the scatter-
ing rate 1/τ provided the order parameter reverses its
sign on the Fermi surface but its angular average is finite
[21]. According to this, the excitation energy spectrum
which is gapless at a low level of scattering can develop
a gap as the scattering rate exceeds some critical value;
i.e., 1/τ > 1/τc. Our surface impedance data on the Pr
doped crystals seem to be remarkably consistent with this
scenario. With increasing Pr concentration, not only are
we introducing pair-breaking magnetic ions but also in-
creasing the scattering rate. While the Tc suppression
can be thought of as due to hole depletion and magnetic
pair-breaking, the enhanced scattering rate may result
in the kind of transition proposed by this theory. Both
the two-slope feature in the transition region and change
in the temperature dependence of the penetration depth
from linear to power-law shown in Fig.1 and Fig.3 can be
reconciled as a manifestation of a transition from a gap-
less state to a superconducting state with a finite gap.

Finally, we would like to remark about the case of
mixed state order parameter symmetry like s + d in the
123 system. In this case, where the order parameter has
line nodes on the Fermi surface, elastic scattering sup-
presses the Tc vigorously and has a dominant influence
over spin-flip scattering. The transition for a linear T
to T4 dependence in λ can be interpreted as the sup-
pression of the d-part of the order parameter, whereas
insensitive to the impurities, s-wave survives. It is to
be noted that our recent microwave experiments on high
quality YBa2Cu3O7−δ single crystals grown in BaZrO3

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crucibles indicate evidence for a multi-component order parameter symmetry \[21,22\].

In conclusion, we have presented the microwave surface impedance for \((Pr_xY_{1-x})Ba_2Cu_3O_7-\delta\) single crystals with \(x\) ranging from 0 to 0.5. Both the surface resistance and penetration depth data indicate strong scattering effects. Novel structure in the superconducting transition region and the temperature dependence of the penetration depth may be consistent with a phase transition from a gapless to finite-gap state governed by the scattering rate.

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FIG. 1. Surface Resistance of \(Pr_xY_{1-x}Ba_2Cu_3O_7-\delta\). The superconducting \(T_c's\) for \(x = 0, 0.15, 0.23, 0.3, 0.4, 0.5\) are 92K, 82K, 71K, 58K, 46K, and 22K, respectively.
FIG. 2. Surface Reactance $X_s$ of $Pr_xY_{1-x}Ba_2Cu_3O_{7-δ}$.

FIG. 3. Low temperature penetration depth $\Delta\lambda(T)$ vs reduced temperature $t = T/T_c$. For $x = 0.15$ and 0.4 the data follows a $t^4$ dependence. Inset shows the data for $x = 0.4$ (solid line) along with a $t^4$ curve (dashed line) for comparison. An approximate $\lambda_0$ is added to each data.