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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Abstract

We report measurements of the surface impedance \(Z_c = R_c + iX_c\) 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 \(R_c(T)\) 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 pair breaking of the Pr. © 1997 Elsevier Science B.V.

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1. Introduction

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 90 K. 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 \(x \sim 0.55–0.6\) \([1,2]\). 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 \(x\) 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) \([2]\). Superconducting electron pair breaking could be produced by potential scattering of mobile holes by the Pr ions if \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) 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 \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) is an \(s\)-or \(d\)-wave...
(spin-singlet) superconductor [3]. 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 $(Ca_{1-x}Pr_{x}Y_{1-x-y})Ba_2Cu_3O_{7-\delta}$ system for $0 \leq x, y \leq 0.2$ (here, mobile holes are generated by Ca and annihilated by Pr [2,4]) and the pressure dependence of $T_c$ in the $(Pr_{x}Y_{1-x})Ba_2Cu_3O_{7-\delta}$ system for $0 \leq x \leq 0.5$ [5,6]). The hole-depletion and pair breaking mechanisms are assumed to originate in the hybridization of the localized Pr4f states and the CuO$_2$ valence band states. The existence of Pr4f-CuO$_2$ valence band hybridization was first proposed on experimental grounds to account for the anomalous pressure dependence of $T_c$ of the $(Pr_{x}Y_{1-x})Ba_2Cu_3O_{7-\delta}$ system [5,6], in analogy with the anomalous behavior of $T_c$ under pressure in superconductors containing Ce impurities such as La$_{1-x}$Ce$_x$ [7]. To the extent that pair breaking is responsible for the depression of $T_c$ in the $(Pr_{x}Y_{1-x})Ba_2Cu_3O_{7-\delta}$ system, it would be necessary to invoke Pr4f-CuO$_2$ valence band hybridization in order to generate a sufficiently strong coupling of the Pr ions to the mobile holes in the CuO$_2$ planes. Except for Ce, the other lanthanide (Ln) ions with partially-filled 4f electron shells do not depress the $T_c$ of YBa$_2$Cu$_3$O$_{7-\delta}$ by a measurable amount; evidently, the Ln4f-CuO$_2$ valence band hybridization and, in turn, the exchange coupling of the Ln ions to the holes in the 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 Gor’kov (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) [7]. Measurements of the low temperature specific heat in the range $0 < x \leq 0.5$ reveal a broad anomaly in the specific heat [8,9]. This anomaly can be described by the sum of a term of the form $C_v(T) = \gamma T$ with an enormous 'heavy-fermion-like' value of $\gamma$ of $\sim 240$ mJ/mol Pr $- K^2$ 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 $x$ [9] or an anomaly associated with antiferromagnetic ordering of the Pr ions [10]. It has been shown that the detailed $T_c$ vs. $x$ curve of the $(Pr_{x}Y_{1-x})Ba_2Cu_3O_{7-\delta}$ 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 $0 \leq x \leq 0.2$ [11]. 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$_{x}Y_{1-x}Ba_2Cu_3O_{7-\delta}$ has a ground state with unusual electronic properties, and which has been proposed theoretically to account for the insulating nature of PrBa$_2$Cu$_3O_{7-\delta}$ [12]. Neutron scattering experiments indicate long range AFM ordering of the Pr moments in the insulating compound PrBa$_2$Cu$_3O_{7-\delta}$ with an unusually high Neél temperature $T_N$ of 17 K [1]. Overall the Pr$_{x}Y_{1-x}Ba_2Cu_3O_{7-\delta}$ 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 [13] and BSCCO [14] 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 ($Z_s = R_s + i X_s$) measurements on a series of Pr$_{x}Y_{1-x}Ba_2Cu_3O_{7-\delta}$ 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.

2. Experiment

The single crystals were grown using a flux-growth method described in an earlier publication.
The Pr concentration $x$ of the single crystals was inferred from their measured $T_c$ values and the $T_c$ vs. $x$ curve of polycrystalline Pr$_{1-x}$Ba$_2$Cu$_3$O$_{y-6}$ samples reported in Ref. [11]. Typical crystals used in our experiments were of size $0.7 \times 0.7 \times 0.05$ 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 4 K to 300 K [16]. This cavity perturbation method has been extensively validated in precision measurements of $R_s$ and $X_s$ in single crystals of cuprate [14,21,22] and borocarbide superconductors [17].

The Nb cavity is maintained either at 4.2 K or below 2 K 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 $\Delta \lambda(T) = \zeta [\lambda(T) - \lambda_b(T)]$ where the geometric factors are determined by the cavity mode, crystal size and location within the cavity. 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.

3. Results and discussion

In Fig. 1, the surface resistance $R_s(T)$ for Pr$_{1-x}$Ba$_2$Cu$_3$O$_{y-6}$ with $x = 0.0, 0.15, 0.23, 0.3, 0.4, 0.5$ are shown. The data are normalized at $R_s(100$ K) to highlight the systematic variation of the surface resistance with increasing Pr concentration. The normal state $R_s(100$ K) 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 $R_s = \sqrt{\omega \mu_0 \rho_n / 2}$, 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 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 $R_s$ for $T \leq 18$ K and the temperature dependence almost mimics the normal state data just above the superconducting transition. This is an important observation which we believe for the first time qualitatively captures the competing effects of magnetism and superconductivity in cuprates as revealed in surface impedance measurements. It should also be pointed out that the presence of exchange interactions due to the Pr-4f moments could also result in enhanced electron–
electron interaction 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 $R_s(T)$ seen for higher Pr doping.

It is to be pointed out that all the anomalous characteristics seen here for the Pr$_{x}$Y$_{1-x}$Ba$_2$Cu$_3$O$_{7-\delta}$ system have been observed by us in our microwave experiments of borocarbide class of magnetic superconductors [17]. In general, a high residual surface resistance, multiple structure in the transition and the low temperature upturn in $R_s$ all seem to be standard electrodynamic characteristics of systems exhibiting co-existence of magnetism and superconductivity. Systematic high frequency experiments on known magnetic superconductors would help further understand the implication of these features.

The normalized surface reactance $X_s(T)$ is shown in Fig. 2. The overall trend is similar to the corresponding $R_s(T)$ 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 15 K higher in temperature. It is not clear whether these features are related to coherence effects. The surface reactance also shows an upturn at low temperature but the onset of this is about 10 K lower than the corresponding onset in $R_s$. The change in reactance is directly related to the change in penetration depth via the relation $X_s = \mu_0\omega\lambda$. In Fig. 3, the low temperature penetration depth extracted from the surface reactance is plotted as a function of reduced temperature ($T/T_c$). Measurement of the absolute value of the penetration depth is not possible with the cavity perturbation...
technique. However, an estimate can be obtained by setting $R_s = X_s$ in the normal state assuming local electrodynamics. An estimated London penetration depth $\lambda_0$ is added to each set of data in Fig. 3.

For the undoped YBCO sample ($x = 0$), the penetration depth is linear in temperature. This linear dependence 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 doping, the temperature dependence of $\lambda$ changes to a power law behavior. For the $x = 0.15$ and 0.4, the best fit to the data is obtained with a $T^4$ term. It is important to note that the data do not show a $T^2$ behavior reported in thin films of YBCO [18] and Zn-doped YBCO single crystals [19]. The change over from $T$ to $T^2$ 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 differences in $R_s$ between the (Zn, Ni) and Pr-doped YBCO. In the case of Zn or Ni-doped samples, although the normal state $R_s$ increases with doping, there is negligible change in the low temperature residual surface resistance. On the contrary, the normal state and residual $R_s$ increase with Pr concentration in $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$. 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 pro-
posed that in layered superconductors it is possible to have a novel phase transition governed entirely by the scattering rate $1/\tau$ provided the order parameter reverses its sign on the Fermi surface but its angular average is finite [20]. 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., $1/\tau > 1/\tau^*$. 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 increasing the scattering rate. While the $T_c$ 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 Figs. 1 and 3 can be reconciled as a manifestation of a transition from a gapless 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 suppresses the $T_c$ vigorously and has a dominant influence over spin-flip scattering. The transition for a linear $T$ to $T^4$ dependence in $\lambda$ can be interpreted as the suppression 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 YBa$_2$Cu$_3$O$_{7-\delta}$ single crystals grown in BaZrO$_3$ crucibles indicate evidence for a multi-component order parameter symmetry [21,22].

In conclusion, we have presented the microwave surface impedance for (Pr$_x$Y$_{1-x}$)Ba$_2$Cu$_3$O$_{7-\delta}$ single crystals with $x$ ranging from 0 to 0.5. Both the surface resistance and penetration depth data indicate strong scattering effects. The 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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