Muon Spin Rotation Study of the Correlation Between T_c and n_s/m^* in Overdoped $Tl_2Ba_2CuO_{6+\delta}$

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The muon spin depolarization rate σ was measured in overdoped $Tl_2Ba_2CuO_{6+\delta}$. $\sigma(T\rightarrow 0)$ was found to decrease proportional to the superconducting transition temperature T_c as doping δ is increased. In the framework of the clean-limit London model, $\sigma(0)\sim\lambda^{-2}\sim n_s/m^*$, this implies that the depression of T_c by overdoping is associated with a decrease of the superconducting condensate density n_s in spite of the increasing normal-state carrier density. This can be largely accounted for in terms of strong pair breaking, which depresses both the condensate density and T_c with increased doping.

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The muon-spin-rotation (μSR) technique provides a powerful tool to measure the magnetic penetration depth λ in type II superconductors [1–5]. λ is derived from the muon spin depolarization rate $\sigma\sim\lambda^{-2}$ which reflects the field distribution in the vortex state in a high external magnetic field. In the clean-limit London model, λ^{-2} is determined essentially by the superconducting condensate density n_s divided by the effective mass m^*. The remarkable result of previous μSR experiments was that, in the low-doping regime, the data appeared to trace a common line in a plot of T_c versus σ_0 [$\sigma(T\rightarrow 0)$] (see dashed line in Fig. 1). Close to optimum doping, where n_s/m^* becomes large, T_c deviates from this line, showing saturation followed by a slight decline with increasing n_s/m^*. This experimental finding was taken as evidence for a high-energy-scale pairing mechanism ($E_{\text{pairing}}\gg E_F$) and suggests a picture of real-space paired bosons, which Bose condense in a common state at T_c [6]. Such a model is able to explain the linear growth of T_c with increasing carrier concentration.

In this Letter we report the first systematic μSR measurements for the heavily overdoped region. We show that n_s/m^* falls to zero as T_c is depressed in overdoped specimens in which the normal-state charge-carrier concentration increases as T_c decreases. The $Tl_2Ba_2CuO_{6+\delta}$ system (Tl-2201) used in this study provides a system in which the strongly overdoped regime is easily accessible. The transition temperature can be varied continuously from about 90 K for $\delta\sim 0$ to 0 K for $\delta\sim 0.1$. Hall measurements clearly demonstrate that additional hole carriers are doped into the CuO_2 planes by the excess oxygen incorporated into the Tl_2O_2 bilayers [7,8]. Three sintered polycrystalline Tl-2201 disks (16 mm in diameter and 2 mm thick) were prepared with transition temperatures of 84, 53, and 13 K by annealing at various oxygen partial pressures and temperatures then quenching into liquid nitrogen. The progressive increase in hole concentration in these samples has been confirmed from resistivity, thermoelectric power, and heat capacity studies. A further sample was obtained from the 53 K sample by charging with hydrogen at 160 °C. It was previously shown that hydrogen acts as an electron donor in the high-T_c systems, compensating the hole carriers necessary for superconductivity [9]. The hydrogen treatment of our sample resulted in an increase of T_c of about 13 to 66 K, which clearly demonstrates the counterdoping of some of the excess hole carriers. The increasing hole concentration, p, was quantified from thermoelectric power (TEP) mea-

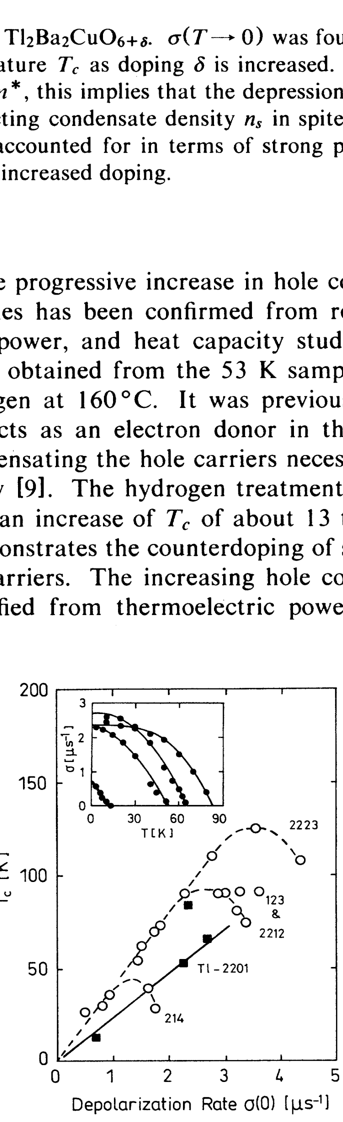

FIG. 1. Relation between T_c and the depolarization rate σ_0. Squares indicate our data on $Tl_2Ba_2CuO_{6+\delta}$ extending into the overdoped region. Open circles represent data taken from Uemura *et al.* on a variety of high-T_c superconductors [1]. Inset: Temperature dependence of the depolarization rate σ for the different $Tl_2Ba_2CuO_{6+\delta}$ samples. The solid lines represent theoretical curves of the form $\sigma(T)=\sigma(0)[1-(T/T_c)^a]$.

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surements made on two of these samples (53 and 13 K). A universal correlation between the room temperature TEP and hole concentration has recently been demonstrated for the high-T_c cuprates [10]. This is linear and negative on the underdoped side and grows exponentially to large positive values on the underdoped side. The negative TEP measured for these Tl-2201 samples is unambiguous evidence for overdoping and using this correlation, the hole concentration has been deduced for the two Tl-2201 samples. The solid square data points in the inset of Fig. 2 show T_c plotted against the thus-calculated values of hole concentration and clearly indicate overdoping. Moreover, the magnitude and temperature dependence of the TEP and the fact that T_c plotted against room temperature TEP is almost identical to that for other overdoped high-T_c cuprates confirms that the TEP is dominated by the CuO_2 planes and no significant contribution arises from the Tl_2O_2 layers. The solid curve in the inset of Fig. 2 is a convenient measure of $T_c(p)$ given by $T_c = T_c(\max)[1-82.6(p-0.16)^2]$ which applies to $La_{2-x}Sr_xCuO_4$ [11] and may possibly be of general applicability [10,11]. p denotes the dimensionless doped hole concentration per planar Cu atom. In the absence of TEP data the 66 and 84 K samples are plotted as open squares on this curve using this parabolic relation. It is not known whether the 84 K sample is underdoped or overdoped. The μSR data for this sample is consistent with underdoping but some decomposition may have occurred in the grain boundaries due to the low oxygen pressure heat treatment.

In the inset of Fig. 1 the temperature dependence of

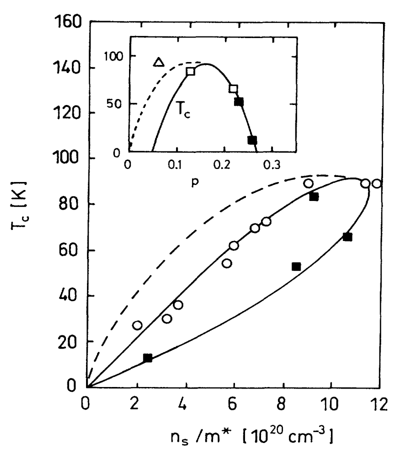

FIG. 2. Inset: Hole dependence of $T_c(p)$ (solid curve) and of $\Delta(p)$ (schematic dashed curve). Squares are T_c for our Tl-2201 samples plotted against p determined from thermoelectric power measurements (solid squares) or fitted to the $T_c(p)$ curve (open squares). T_c plotted as a function of n_s/m^* where m^* is the electron mass enhancement in units of m_e. Squares: $Tl_2Ba_2CuO_{6+\delta}$; circles: $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$. Solid curve: Pair breaking model based on $T_c(p)$; dashed curve: based on $\Delta(p)$. The difference between dashed and solid curves arises from localization.

the transverse-field muon spin depolarization rate for the different samples is shown. Each sample was mounted in a He gas flow cryostat with the disk face perpendicular to the incoming muon beam direction $\hat{\mathbf{z}}$ and normal to the initial muon spin polarization. The data were taken by cooling the samples in an external field of 3 kG, applied parallel to $\hat{\mathbf{z}}$. The measured spectra were analyzed assuming a Gaussian distribution of internal fields, yielding the Gaussian depolarization rate $\sigma(T) \sim \lambda^{-2}(T)$. This approximation of the intrinsic field distribution of a polycrystalline type II superconductor was shown previously to give satisfactory results for the magnetic penetration depth [2,12]. From such measurements, two important parameters can be determined, the zero-temperature value σ_0, which relates to the superconducting condensate density and an exponent α describing the temperature dependence of $\sigma(T)$, which we fitted to the trial function

$$\sigma(T) = \sigma_0[1-(T/T_c)^\alpha]\,. \qquad (1)$$

In all previous studies for the underdoped regime σ_0 increases with the number of charge carriers. There, the condensate density $n_s(T \to 0)$ (as measured by σ_0) is directly related to the increase of normal state carrier density n. If this were still true for the overdoped regime in the $Tl_2Ba_2CuO_{6+\delta}$ system the sample with the highest carrier concentration, i.e., the 13 K sample, should have the highest depolarization rate at $T=0$. The inset of Fig. 1 shows this is obviously not the case. σ_0 reaches a maximum then decreases with increasing density of normal-state charge carriers. By plotting T_c versus σ_0 for the three overdoped Tl-2201 samples we find a linear correlation. This can be seen in Fig. 1 by the squares representing our data on overdoped $Tl_2Ba_2CuO_{6+\delta}$ and the solid line connecting these data points. The only exception is the 84 K sample, which falls on the curve measured by Uemura *et al.* This suggests that this sample was slightly overdoped. Our data thus extends the universal correlation between T_c and σ_0 to the overdoped regime, and suggests that, even though the normal-state carrier density n increases, the superconducting condensate density decreases. This is incompatible with the BCS picture in which $n_s(T=0) \sim 1/2n$.

We emphasize that our conclusions are significant because of evidence from a variety of measurements that the Tl-2201 system is a homogeneous single-phase overdoped material. All the structural irregularities are associated with the doping centers inside the nonsuperconducting TlO layers [8], which are remote from the CuO_2 planes. The transport properties progress smoothly towards more and more metallic behavior with increasing hole doping from excess oxygen [7,13,14]. Even the transition from superconductor to metal shows no discontinuous behavior. The resistivity of these samples progressively decreases and develops a normal metallic T^2 behavior. The residual resistance for low temperatures decreases with increasing T_c [7]. Susceptibility measurements for $T < T_c$ indicate that the superconducting transition remains sharp even in samples with T_c values as low as 10 K [7]. We therefore conclude that the Tl-2201 system has very homogeneous properties for the whole overdoped region.

Heat capacity studies provide useful insight into the present data. High precision differential heat capacity measurements [15] were carried out as a function of oxygen content on $Tl_2Ba_2CuO_{6+\delta}$ synthesized from the same batch as used in the present μSR experiments. The superconducting pair density n_p was estimated from the jump in heat capacity at T_c in units of k_B per unit volume. This falls away rapidly in the overdoped region as T_c is reduced. If the pair density is estimated from the normal-state carrier density n by $n_p \sim (\Delta/E_F)n$ and a 2D electron gas model is used for the Fermi energy E_F then n_p should scale with T_c. In fact, n_p falls more rapidly than T_c does. This rapid decline in both n_p and n_s can be viewed as arising from a diminished rigidity of the condensate wave function due to pair breaking in the overdoped region. This is borne out by the low temperature value of $\gamma = C_p/T$ which progressively rises to large nonzero values with overdoping indicating pair-broken states within the BCS gap [15]. Moreover, $La_{2-x}Sr_xCuO_4$ and $Tl_{0.5}Pb_{0.5}Sr_2Ca_{1-x}Y_xCu_2O_7$ [16] both exhibit the same rapid decline in pair density in the overdoped region indicating a common pair-breaking behavior in superconducting cuprates with widely different optimum T_c values (39 and 108 K, respectively). T_c is evidently depressed by pair breaking while entropy contributions above T_c (from finite-lifetime fluctuations in pair density) reduce the magnitude of the jump in heat capacity and hence the apparent pair density.

Our view that n_s is depressed due to pair breaking complements a wider cluster of observations which present a clear picture of near gapless superconductivity in the HTSC cuprates arising from pair breaking. These include the absence of far-infrared transmission enhancement at the gap frequency [17], absence of the NMR coherence peak at T_c [18], tunneling conductance at small voltages within the gap [19], the persistence of IR absorption and Raman scattering within the gap at low temperatures [20], and the temperature independence of the spectral range of the reflectivity enhancement within the gap [21]. Heat capacity studies on Zn-substituted $YBa_2Cu_3O_{7-\delta}$ show that $\gamma(T=0)$ rises above zero for very small levels of substitution indicating that this compound near $T=0$ is close to being gapless [22]. An alternative interpretation is that in the overdoped region the carriers cross over from hole states to electron states so that continued hole doping depresses the carrier concentration. The transport properties do not support this view. For Tl-2201 the resistivity continues to fall with overdoping and the Hall number continues to rise and there is no change in sign [7]. The TEP in both the underdoped and overdoped regions is characterized by an essentially constant linear negative slope with a positive intercept at $T=0$ which falls smoothly with doping and does not become negative until superconductivity is suppressed [10]. The anomalous depression of the Meissner fraction with overdoping in Tl-2201 [7] has no natural basis in a change in carrier type but reinforces our proposed pair-breaking scenario.

A satisfactory model to explain our data has to take into account the symmetrical behavior of T_c, n_s, α, and n_p around optimum doping and the fact that the energy gap Δ does not scale with T_c. A first approach is to treat the underdoped and overdoped sides on the same footing by assuming a constant pair-breaking scattering length, l_b, on both sides.

We envisage a pairing mechanism, possibly magnetic in origin [23], which provides an approximately parabolic dependence of the energy gap on hole concentration as shown by the dashed curve in the inset of Fig. 2. Long-range phase coherence of the superconducting order parameter does not develop, because of localization effects, until a finite doping level. Thus, as indicated by Raman [24] and heat capacity [16,25] studies, the energy gap is already well developed on the underdoped side when T_c rises from zero as shown by the solid curve in the inset of Fig. 2. T_c and Δ probably both maximize near optimum doping. Consider the consequences of moving away from optimum doping on either side. Once Δ falls near the characteristic pair-breaking energy the effective penetration depth is given by

$$\lambda^2 = \lambda_L^2(\xi_0/l_b)\,, \tag{2}$$

where $\lambda_L \sim (n/m^*)^{-1/2}$ is the London penetration depth and ξ_0 the $T=0$ coherence length. λ is the analog of the dirty-limit penetration depth and λ rises above λ_L due to pair breaking which reduces the effective condensate density. In the absence of pair-breaking $\xi = \hbar v_F/\pi\Delta(0) = 2\hbar v_F/\pi\eta k_B T_c$, where v_F is the Fermi velocity of the carriers and η a small number (3.52 for weak coupling BCS). Even though T_c does not scale with $\Delta(0)$ in the presence of pair breaking we may assume that the pair broken coherence length still preserves this inverse dependence on T_c and Eq. (2) becomes

$$\left(\frac{n_s}{m^*}\right)_{\text{effective}} = \frac{n}{2m^*}\,\frac{\pi\eta k_B l_b}{2\hbar v_F}\,T_c\,. \tag{3}$$

This is the observed scaling behavior, independent of anisotropy or dimensionality, provided that l_b is a weak function of hole doping. We note also that n is a weak implicit function of T_c. There thus appears to be a domain near optimum doping where pair breaking is weak and the penetration depth shrinks to near its minimal London value which at $T=0$ is determined by the normal-state carrier density. In this domain λ^{-2} continues to grow with increasing carrier density (even though T_c falls) until pair-breaking interactions significantly reduce the pair lifetime and λ^{-2} then scales with T_c again. This can be quantified as follows. We approximate the entire domain using the relation $\lambda^2 = \lambda_L^2(1+\xi_0/l_b)$. This is appropriate for the limits of very weak and very strong pair breaking and provides a useful guide for the crossover. Neglecting localization we may approximate n (in λ_L) by $2p/a^2c$ where p is the hole concentration while a and c are the lattice parameters. The Fermi velocity may be approximated from the 2D electron gas using $v_F \approx \sqrt{2\pi\hbar^2 n/m^{*2}}$. Fitting the μSR data in the linear domain of Eq. (2) with a constant pair-breaking length gives $l_b \sim 60.0$ Å which is entirely reasonable. This pair-breaking scattering length must not be confused with the transport mean free path of the carriers, which was found to be in the order of several hundred Å [26]. The normal state transport properties were argued to be governed by the spin dynamics within the CuO_2 planes and the suppression of these fluctuations by the formation of spin singlets results in a diminished scattering of the carriers [27,28]. Over the entire range the condensate density has the form

$$n_s/m^* \approx p[1+\sqrt{p}(T_0/T_c)]^{-1} \tag{4}$$

and this is fitted to the μSR data in Fig. 2. In the absence of underdoped data for Tl-2201 we have simply plotted the underdoped data for $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$ up to the onset of the plateau in each case. The fit can be seen to be very reasonable. The dashed curve is the expected curve when the hole-dependent energy gap $\Delta(p)$ (shown by the dashed curve in the inset of Fig. 2) is used instead of T_c. The fall of the solid curve (T_c) away from the dashed curve in both the inset and the main figure is presumed to arise from localization.

A second, more realistic approach is to recognize that the depression in condensate density occurs via a variable l_b. Thus pair breaking may be relatively weak on the underdoped side but l_b contracts on the overdoped side as the density of pair-breaking interactions grows. In this regard it is notable that Oda *et al.* [29] have shown that the decline in T_c for $La_{2-x}Sr_xCuO_4$ and $La_{2-x}Ba_xCuO_4$ is observed to follow the rising magnitude in Curie term due to local moments in good agreement with the Abrikosov-Gork'ov theory for magnetic depairing.

Another interesting trend in our data shows up in the exponent α, which falls from 3.4 for $T_c = 84$ K, to 2.3 for $T_c = 66$ K, to 1.8 for $T_c = 53$ K, to 1.2 for $T_c = 13$ K. In optimally doped high-T_c-superconductors α values around 4 are observed [2] as occurs in the two-fluid model and suggests strong coupling [30]. Mikhailowsky *et al.* [31] shows that a combination of strong coupling and high transition temperature results in thermal pair breaking and they obtain $\alpha = 4$ for the temperature dependence of the density of normal carriers, of the penetration depth and the optical conductivity. According to these authors the states within the gap account for the two-fluid phenomenology and we suggest that the progressive magnetic pair breaking on the overdoped side broadens the gap edge and therefore progressively weakens the temperature dependence and reduces α.

In this paper we presented the first experimental evidence for a correlation between T_c and the superfluid density n_s in the overdoped regime. Our data clearly show that the *depression* of T_c in the overdoped region is accompanied by a *decrease* of the measured depolarization rate σ_0 and thus of n_s/m^* even though the normal-state measurements clearly indicate an *increase* in normal-state carrier concentration with doping in this region. We observe a linear depression in $\sigma_0 \propto n_s/m^*$ with T_c which is explicable in terms of pair breaking and complements a growing body of evidence for the prominence of pair breaking and nearly gapless superconductivity in the high-T_c cuprates.

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