Muon Spin Relaxation Studies of Zn-Substitution Effects in High-T_c Cuprate Superconductors

B. Nachumi, A. Keren, K. Kojima, M. Larkin, G. M. Luke, J. Merrin, O. Tchernyshöv, and Y. J. Uemura
Physics Department, Columbia University, New York, New York 10027

N. Ichikawa, M. Goto, and S. Uchida
Department of Superconductivity, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan
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We have performed transverse-field muon spin relaxation measurements of the Zn-substituted cuprate high-T_c superconductors: $La_{2-x}Sr_x(Cu_{1-y}Zn_y)O_4$ and $YBa_2(Cu_{1-y}Zn_y)_3O_{6.63}$. The superconducting carrier density/effective mass n_s/m^* ratio at $T \rightarrow 0$ decreases with increasing Zn concentration, in a manner consistent with our "swiss cheese" model in which charge carriers within an area $\pi\xi_{ab}^2$ around each Zn are excluded from the superfluid. We discuss this result in the context of Bose condensation, pair localization, and pair breaking. [S0031-9007(96)02011-X]

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Zn substitution for Cu in the high-T_c cuprates dramatically suppresses superconductivity. In both $La_{2-x}Sr_x(Cu_{1-y}Zn_y)O_4$ (La-214) and $YBa_2(Cu_{1-y} \times Zn_y)_3O_{6+x}$ (Y-123) compounds, an impurity concentration y of 2–3 at. % (per Cu) reduces T_c to half or less the value for unsubstituted systems over a wide region of hole doping level x [1–3]. In Y-123 which has both CuO_2 planes and CuO chains, divalent Zn or Ni atoms are believed to selectively substitute the planar Cu sites [4] without changing the charge doping. In a lattice of antiferromagnetically coupled Cu moments, nonmagnetic Zn^{2+} ions may cause an effect similar to that of magnetic impurities in nonmagnetic environment. NMR studies of spin susceptibility in Zn-substituted Y-123 (Y-123:Zn) systems have shown that Zn induces localized moments on neighboring copper ions [4,5]. In the phase diagram as a function of hole doping x in Y-123 [2,4], Zn substitution reduces the superconducting region, while enlarging the region with a spin-glass-like disordered-magnetic ground state between the antiferromagnetic and superconducting regimes.

Investigations of the suppression of superconductivity in Zn-substituted cuprates may illuminate the mechanisms of high-T_c superconductivity. So far, models for Zn-substituted cuprates have focused on the effects of magnetic and potential pair-breaking scattering on the T_c of d-wave superconductors [6–8]. However, these theories fall somewhat short in explaining observed results. The T_c reduction in irradiated samples of Y-123 is fit by the pair-breaking theory only if the pair-breaking scattering rate is $\frac{1}{3}$ of the transport scattering rate [9]. The same situation exists for Zn-substituted systems, as we shall see later. Recently, Fukuzumi *et al.* [3] found that the a-b plane sheet resistance approaches a universal 2D sheet resistance $h/4e^2$ when superconductivity disappears with increasing Zn concentration in originally underdoped Y-123 and La-214 systems. This observation suggests that the suppression of T_c may be related to the localization of paired electrons.

Transverse field muon spin relaxation (TF-μSR) is a powerful method for studying type-II superconductors. The muon spin relaxation rate σ is related to the magnetic field penetration depth λ, and consequently to n_s/m^* (superconducting carrier density/effective mass), as $\sigma \propto \lambda^{-2} \propto n_s/m^*$ [10]. Note that n_s/m^* represents a characteristic energy scale of superconducting carriers [11]. In Y-123, La-214, and many other cuprate superconductors, we have found "universal correlations" between T_c and $\sigma(T \rightarrow 0) \propto n_s/m^*$: T_c increases linearly with n_s/m^* with increasing carrier doping in the underdoped region, then shows saturation in the optimum-T_c region [10,11]. In the overdoped Tl-2201 systems, both T_c and n_s/m^* *decrease* with increasing hole doping [12,13], bringing the trajectory in the T_c versus σ plot back to the origin. Combining (1) the pseudo gap behavior which suggests formation of preformed pairs above T_c and (2) the universal correlations in the underdoped and optimum region, one can develop a model for high-T_c cuprates in terms of evolution from Bose-Einstein to BCS condensation [14].

In this paper we report μSR measurements of the Zn-substituted Y-123 ($6 + x = 6.63$) and La-214 systems ($x = 0.15$ and 0.2). We study the variation of n_s/m^* (in addition to that of T_c) as a function of Zn concentration y and compare with various theoretical models for the suppression of superconductivity. In particular, we have found that the reduction of n_s/m^* with increasing y occurs in a manner consistent with a model in which charge carriers in the region of $\pi\xi_{ab}^2$ (ξ_{ab} is the in-plane coherence length) around each Zn impurity on the CuO_2 planes are excluded from the superconductivity. Our preliminary results for La-214:Zn were presented recently [15].

Recently Bernhard *et al.* [16] reported μSR studies in Y-123:Zn and an overdoped La-214:Zn. Their experimental data are qualitatively consistent with the results in the present paper. Treating impurity concentration y as an implicit parameter, they interpreted their results to be consistent with a pair-breaking model in the unitary limit.

In this paper we show that the pair-breaking model is insufficient to account for the dependence of T_c (and n_s) on the planer Zn concentration.

In transverse external magnetic fields H ($H_{c1} \ll H \ll H_{c2}$), the depolarization rate σ of the TF-μSR signal in type-II superconductors is proportional to the width ΔH of the field distribution in the sample, leading to

$$\sigma \propto \Delta H \propto \lambda^{-2} = (4\pi n_s e^2/m^* c^2)[1/(1 + \xi/l)]. \quad (1)$$

In clean-limit superconductors whose mean free path l is sufficiently longer than the coherence length ξ, one obtains a simple relationship $\sigma \propto \lambda^{-2} \propto n_s/m^*$. The constant of proportionality between σ and λ^{-2} depends on the symmetry and regularity of the flux lattice, which we assume to be independent of the system in this paper. For ceramic samples of highly anisotropic cuprate superconductors, the angular average of the penetration depth is dominated by the *a-b* plane values λ_{ab}, thus reflecting the in-plane effective mass m^*_{ab} and coherence length ξ_{ab}. Assuming the same angular averaging for different specimens, $\sigma(T \rightarrow 0)$ can be used to study system dependence of the ground state values of n_s/m^*_{ab}. The temperature at which σ rises significantly above its $T > T_c$ value marks the onset of superconductivity.

The samples were prepared by a standard solid-state reaction described elsewhere [17]. The μSR measurements were performed at the M15 and M20 surface muon channels at TRIUMF. Most of the data points were taken using a standard Janis gas-flow cryostat (a low-T limit of 2.2 K), with the samples mounted on pressed rust powder to minimize backgrounds. The measured asymmetry $A(t)$ was fit to a phenomenological form

$$A(t) = A_0 \exp(-\sigma^2 t^2/2) \cos(\omega t + \phi), \quad (2)$$

where A_0 is the initial asymmetry of the decaying muons, and ω is the modal frequency in the sample. This form is appropriate for the line shape in a ceramic sample, where the typical Abrikosov lattice line shape has been broadened into a Gaussian-like peak around ω.

In Fig. 1 we show the temperature dependence of σ for the La-214 ($x = 0.15$) and Y-123 ($6 + x = 6.63$) series. Zn substitution markedly reduces $\sigma(T \rightarrow 0)$ by a factor of $\frac{2}{3}$ for $y = 0.005$. Similar results are obtained in the La-214 ($x = 0.20$) series. The ($x = 0.15, y = 0.01$) sample exhibits weak static magnetic order below 5 K. This magnetism is manifested as a divergence of $\sigma(T)$ below 5 K and was confirmed by zero-field (ZF) μSR measurements. ZF μSR on the La-214 ($x = 0.20, y = 0.01$), ($x = 0.15, y = 0.005$), and Y-123 ($y = 0.01$) samples reveals no indications of static magnetic order down to 2.5 K.

To estimate ξ_{ab}/l in our specimens, we assumed the density of states for a two-dimensional Fermi gas, the Sommerfeld parameter γ derived from specific heat measurements [18] and the scattering time τ inferred from resistivity measurements [3], and obtained $l = 52$, 59, and 101 Å for the La-214 ($x = 0.15, y = 0.01$), ($x = 0.20, y = 0.01$), and Y-123 ($6 + x = 6.63, y = 0.01$), respectively. These lengths increase with decreasing y. $H_{c2} = 63.5$ T for La-214 ($x = 0.15$) was derived from conductivity measurements on Zn-free crystals [19], where $H = 61$ T completely suppressed the superconductivity at $T/T_c = 0.04$. This gives $\xi_{ab} = 22.7$ Å for La-214. Assuming an empirical trend $H_{c2}(T = 0) \propto T_c$, we estimate $\xi_{ab} = 18.3$ Å for the underdoped Y-123. Hence these samples fall near the clean limit.

In Fig. 2 we plot T_c versus $\sigma(T \rightarrow 0)$ for the Zn-substituted series, without corrections for ξ/l, along with the data for other pure samples of La-214, Y-123, and the overdoped Tl-2201 systems. The La-214 points which start on the overdoped branch move toward the "universal" underdoped line, while the Y-123 points which start out on the universal line shift along the line toward the origin. Thus the trajectory in Fig. 2 for Zn-substituted systems follows the behavior of pure systems with varying carrier doping. These results strongly suggest that, regardless of charge or impurity

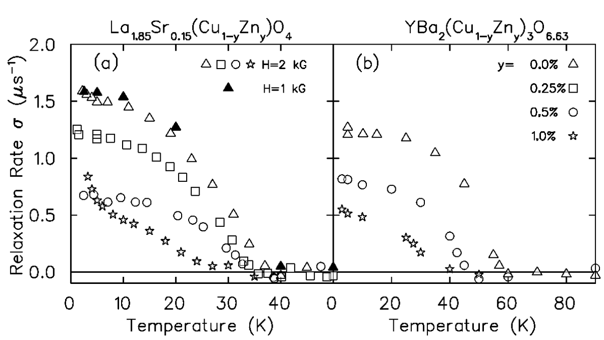

FIG. 1. (a) The TF-μSR relaxation rate σ as a function of temperature for the La-214 ($x = 0.15$) series, and (b) for the Y-123 ($6 + x = 6.63$) series.

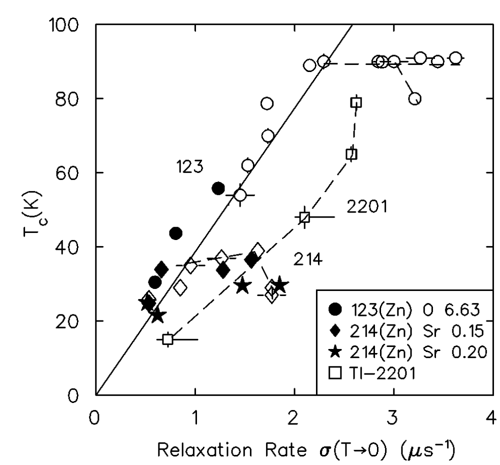

FIG. 2. A plot of the muon spin relaxation rate $\sigma(T \rightarrow 0)$ versus T_c for Zn-substituted (closed symbols; including $y = 0$ reference samples) and pure (open symbols) La-214 and Y-123 systems. The solid line is the "universal" line for the underdoped cuprates found in [10]. Also included are the results for overdoped Tl-2201 systems [12].

doping, it is the parameter n_s/m^* that determines T_c of the La-214 and Y-123 systems.

To study the dependence of n_s/m^* and T_c on Zn concentration, it is important to plot the results against the planar Zn concentration y_{ab}. For Y-123, y_{ab} is 1.5 times larger than y [3,4]. Figure 3 shows such plots in a reduced scale relative to the values in the unsubstituted pure systems. The results for the two La-214 series are nearly identical, in both $\sigma \propto n_s/m^*$ [Fig. 3(a)] and T_c [Fig. 3(b)], for all of the measured y_{ab} values. Similar trends have been seen in measurements of the superconducting plasma edge [20] in the *c*-axis optical reflectivity. The reduction of n_s/m^* [Fig. 3(a)] for Y-123 occurs more slowly than for La-214 with increasing y_{ab}.

In Fig. 3(b) the $T_c/T_{c;\mathrm{pure}}$ points for all the three series follow an approximately common line. This feature is consistent with the results of Fukuzumi *et al.* [3], who found that $T_c/T_{c;\mathrm{pure}}$ for underdoped cuprate systems, plotted against the residual *a*-*b* plane resistivity ρ_{ab}, follows a universal line. Since $\rho_{ab} \propto y_{ab}/n$ [3] in the unitary scattering limit, and the transport carrier density n (per planar Cu) for the underdoped Y-123 is about the same as that of La-214 with $x = 0.15$, $T_c/T_{c;\mathrm{pure}}$ for these two series follows the same behavior whether plotted against y_{ab} or ρ_{ab}. Regarding the normal-state charge transport, Fukuzumi *et al.* [3] found $n \sim x$ for La-214 ($x = 0.15$) and $n \sim (1 - x)$ in overdoped La-214 ($x = 0.2$) systems. This difference caused markedly different trajectories of $T_c/T_{c,\mathrm{pure}}$ lines for these two La-214 series when plotted versus ρ_{ab} (Fig. 3 of Ref. [3]), although they show impressively similar behavior when plotted versus y_{ab} in Fig. 3(b).

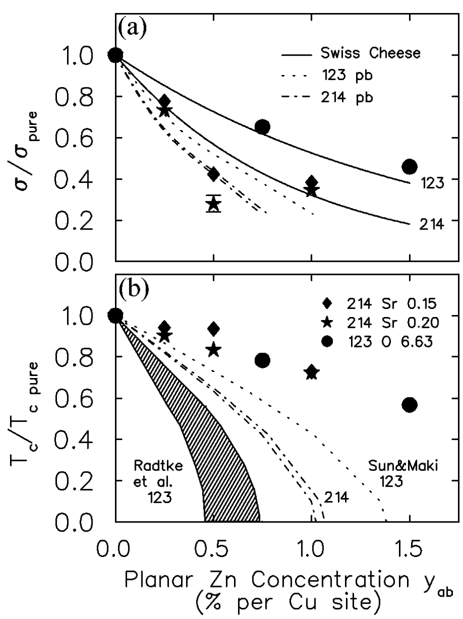

FIG. 3. The dependence of (a) the relaxation rate $\sigma(T \rightarrow 0) \propto n_s/m^*$ and (b) T_c of La-214 ($x = 0.15$, 0.20) and Y-123 ($6 + x = 6.63$) on the concentration y_{ab} of Zn on the CuO_2 planes. In both (a) and (b), the vertical axis is normalized by the values for pure ($y_{ab} = 0$) systems. The solid lines in (a) show the prediction of the swiss cheese model. The broken lines in (a) and (b) show the prediction of the pair-breaking model of Sun and Maki [8], and the shaded area in (b) of Radtke *et al.* [6].

To account for the reduction of n_s/m^* with increasing y_{ab}, we propose a "swiss cheese" model in which charge carriers in a given area around each Zn impurity are excluded from superconductivity. There are several observations which suggest that the electronic structure on the CuO_2 plane involves such a separation of normal and superconducting regions in real space. They include: (1) the T-linear component of the specific heat remains finite at $T \rightarrow 0$ in Zn-substituted systems, and the residual γ increases with increasing y [21], suggesting an increasing ungapped volume fraction even below T_c; and (2) NMR results [4,5] show that the nearest neighbor Cu sites around Zn impurity carry localized moments with a spin susceptibility different from that of other bulk Cu atoms in the CuO_2 planes.

Let us assume that the superconducting wave function is forced to zero at the edge of each Zn impurity. Superconductivity recovers at a radius ξ_{ab}, similar to the response outside a flux vortex. In our model, each Zn removes the carriers in a region $\pi\xi_{ab}^2$ from n_s. The remaining superconducting region resembles a slice of swiss cheese. At first, n_s decreases linearly with y_{ab}, but then tends to saturate as the Zn-affected areas overlap at larger y_{ab}. Analytically, this is given as

$$n_s(y_{ab})/n_s(0) = \Pi_{i=1}^{y_{ab}V_{\mathrm{plane}}}[1 - \beta/(V_{\mathrm{plane}} - ia^2)], \quad (3)$$

where $\beta \approx \pi\xi_{ab}^2/a^2$ is the number of lattice sites where the superconductivity is suppressed, a is the *a*- or *b*-axis lattice constant, and V_{plane} is the number of lattice sites in a plane. The solid lines in Fig. 3(a) show the calculated results for La-214 series with $\xi_{ab} = 18.3$ Å (we assumed that ξ_{ab} is approximately the same for $x = 0.15$ and 0.2), and underdoped Y-123 series with $\xi_{ab} = 22.7$ Å. These two lines, calculated without any adjustable fitting parameter, agree well with the experimental results. This calculation, however, should still be regarded as approximate, since we did not include the possible change of ξ_{ab} with increasing y_{ab}.

Figure 3 also shows predictions from pair-breaking theories for *d*-wave superconductors. Sun and Maki [8] calculated the behavior of n_s and T_c for a *d*-wave superconductor as a function of the scattering rate $\Gamma = n_i/\pi N(0)$ where n_i is the impurity concentration and $N(0)$ the normal-state density of states at the Fermi level. The broken lines in Fig. 3 represent their results with $N(0)$ obtained from specific heat results [18]. Radtke *et al.* [6] also calculated the variation of T_c as a function of the residual *a*-*b* plane resistivity ρ_{ab}: They found that $T_c/T_{c;\mathrm{pure}}$ follows an approximately universal behavior for systems with various $T_{c;\mathrm{pure}}$ if plotted against a parameter $\alpha \propto \rho_{ab}n/T_{c;\mathrm{pure}}$. Since the underdoped Y-123 system and the $T_c = 90$ K Y-123 system have approximately the same $n_s/T_{c;\text{pure}}$, we replot their results for the latter so as to represent the results for the underdoped Y-123 system, drawn as the shaded region in Fig. 3(b). Both of these pair-breaking estimates predict dependences of n_s and T_c as a function of y_{ab} substantially stronger than those observed. Similar disagreement is apparent in the results in irradiated Y-123 systems [9]. The pair-breaking theories predict an increasing slope with increasing y_{ab} in both T_c and n_s, which contradicts the observed trend.

Liquid He in porous media exhibits the reduction of the superfluid density and T_c with decreasing effective coverage [22]: T_c is approximately proportional to the superfluid density within a given bulk volume. This behavior is analogous to the monotonic, and nearly linear relationship between T_c and n_s/m^* in underdoped, Zn-substituted, as well as overdoped cuprate systems shown in Fig. 2. Zn impurities may effectively create "porous" media for the superfluid in the cuprates. The reduction of n_s/m^* with increasing carrier doping in overdoped cuprates can be interpreted by assuming a spontaneous microscopic phase separation (situation similar to the swiss cheese model) between superconducting and nonsuperconducting regions [12,14]. These considerations suggest that T_c in all these systems may be determined by Bose condensation: See Refs. [14,23] for more details of this point.

Possible relevance to Bose condensation can be found also in the disappearance of superconductivity in underdoped La-214:Zn and Y-123:Zn at $\rho_{ab} = h/4e^2$, the critical resistivity expected for localization of (preformed) charge pairs [3]. This result is analogous to superconductor-insulator transitions observed in thin films of Pb, Bi [24], in which T_c decreases linearly with increasing inverse film thickness $1/d$. Note that both $1/d$ in the films and $\rho_{ab} \propto y_{ab}$ in the cuprates represent sheet resistance. In both systems, T_c is essentially determined by the amount of superfluid within a given bulk volume.

In summary, we have presented the μSR results in Zn-substituted cuprate systems. The dependence of n_s/m^* and T_c on y_{ab} can be well explained by the swiss cheese model. The existing pair breaking models provide less satisfactory accounts for the observed results. The effect of Zn substitution has been often discussed [16] in a plot of T_c versus n_s, where the y_{ab} dependence becomes implicit. In the present work, we emphasized the difference between various theoretical models with the explicit y_{ab} dependence in Fig. 3.

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