

Clear distinction between the underdoped and overdoped regime in the T_c suppression of Cu-site-substituted high- T_c cuprates

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The T_c suppression by Cu-site substitution has been studied in a wide range of carrier concentrations p , from the underdoped regime to the overdoped regime, using sintered polycrystals of $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x(\text{Cu}_{1-z}\text{M}_z)_2\text{O}_{8+\delta}$ with $x=0$ and $x=0.3$ and under variation of δ . The carrier-dependent strength of the T_c suppression by substituting $M=\text{Fe}, \text{Co}, \text{Ni}, \text{Zn}$ for Cu is measured. In the overdoped regime, we find T_c scaling as $T_c(p,z)/T_c(p,0)=g(z)$ with a p -independent function $g(z)$, whereas in the underdoped regime $T_c(p,z)/T_c(p,0)$ is strongly p dependent. Replotting data of various publications on the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system and comparison with the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ system demonstrate the universality of this distinction between the two regimes in p -type high- T_c cuprates. The scaling behavior is discussed with respect to Born-limit and unitarity-limit scattering.

Various kinds of measurements, such as muon spin relaxation (μSR),¹ nuclear magnetic resonance (NMR)² and thermoelectric power,³ have shown physically distinct behavior between the carrier-underdoped and overdoped regime of p -type high- T_c cuprates. As the carrier (hole) concentration per Cu, p , increases, T_c increases in the underdoped regime until an optimum value, T_c^{opt} , is reached at $p=p^{\text{opt}}$, and then decreases in the overdoped regime ($p \geq p^{\text{opt}}$). Furthermore, it has been shown that the p dependence of T_c/T_c^{opt} is universal for virtually all p -type high- T_c cuprates,^{4,5} and may be expressed as

$$T_c(p) = f(p)T_c^{\text{opt}}. \quad (1)$$

The shape of $f(p)$ is sometimes described as a negative parabola,⁴ or as a function with a flat optimum.⁵ At present, however, its physical origin is poorly understood and probably crucial to the understanding of high- T_c superconductivity.

To investigate the mechanism of high- T_c superconductivity, Cu-site substitution has already been proven to be a powerful tool. However, there are only few reports on the carrier dependence of the T_c suppression by Cu-site substitution in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (La-124) (Refs. 6–8) and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Y-123) (Refs. 7 and 9) systems. To our knowledge, there are none in the $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+\delta}$ (Bi-2212) system. In the latter, the carrier (hole) concentration can be varied by substituting Y^{3+} for Ca^{2+} and also by changing the amount of excess oxygen δ . Requiring charge neutrality, one formally obtains $p = \delta - x/2 - p'$, where p' refers to the bismuth valence $\text{Bi}^{3+p'}$.

In this paper we investigate $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x(\text{Cu}_{1-z}\text{M}_z)_2\text{O}_{8+\delta}$ with $x=0$ and $x=0.3$ and various values of δ , where M stands for various transition metals such as Fe, Co, Ni, or Zn. The sintered polycrystals have been synthesized by an usual solid-state reaction method, starting from metal oxides and carbonates in the ratio of $[\text{Bi}]:[\text{Sr}]:[\text{Ca},\text{Y}]:[\text{Cu},\text{M}] = 2:2:1:2$. The value of δ was changed by annealing the sintered samples in flowing O_2 or N_2 gas at 350–600 °C for 24

hours. The lowest oxygen content in the case of $x=0.3$ was obtained by annealing the samples at 866 °C/24 hours in air and quenching into liquid N_2 . The oxygen content was estimated from iodometry analysis and weight change. As a criterion of T_c we chose a 50% value of the normal resistivity at the superconducting transition.

In the case of $x=0$, we chose $M=\text{Fe}, \text{Co}, \text{Ni}$, and Zn as substituents. Maeda *et al.*¹⁰ reported for $\text{Bi}_2\text{Sr}_{1.8}\text{Ca}_{1.2}(\text{Cu}_{1-z}\text{M}_z)_2\text{O}_{8+\delta}$ that the solubility limit for $M=\text{Ni}, \text{Zn}$ is at $z=0.02$ and 0.015 , respectively, indicated by a sharp kink in the z dependence of T_c . We also observed this sharp kink for $M=\text{Ni}, \text{Zn}$ and observed a weak kink for $M=\text{Fe}, \text{Co}$ in the vicinity of $z=0.02$. This suggests that above this concentration the substituents only partly occupy the Cu sites, despite powder x-ray diffraction patterns showing no impurity phases caused by the substitution until much higher concentrations.

In the case of $x=0.3$, we investigated only compounds with $M=\text{Co}$ and Zn. We could not detect any impurity phase for $z \leq 0.08$ ($M=\text{Co}$) and $z \leq 0.06$ ($M=\text{Zn}$). Only in the latter case, a kink appeared at $z=0.02$ in the z dependence of T_c .

Generally, in high- T_c cuprates $T_c(z)$ is also a function of p and basically linear in a wide range of z , and therefore can be described at least for small concentrations as

$$T_c(p,z) = T_c(p,0)(1 - z/\bar{z}_c). \quad (2)$$

Here, $\bar{z}_c = T_c(p,0) \lim_{z \rightarrow 0} |dT_c(p,z)/dz|^{-1}$ is the extrapolated critical concentration, where superconductivity vanishes upon substitution. Although for $T_c \rightarrow 0$ deviations from linearity are expected from theory¹¹ and sometimes are observed in terms of a positive or negative curvature (Ref. 12), $T_c(z)$ turns out to be remarkably linear in Y-123 (Ref. 9) and in our Bi-2212 samples below the solubility limit. Because of the solubility limit, the real critical concentration z_c is often experimentally not accessible and we therefore focus in the following on \bar{z}_c defined above.

In general, \bar{z}_c also is a function of p and dependent on the substituent chosen. This has been demonstrated by Liang

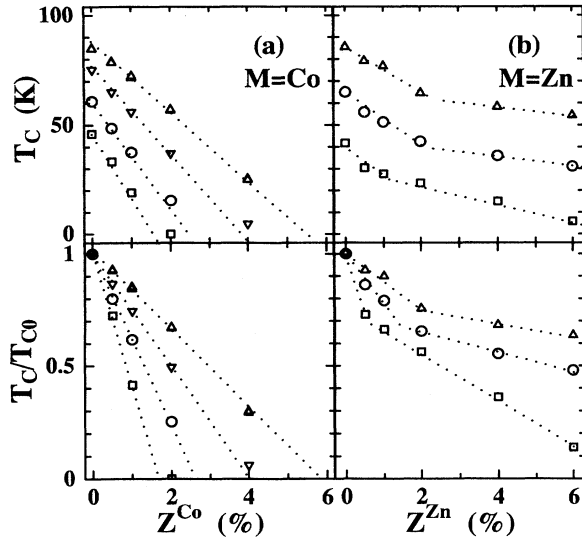


FIG. 1. Upper charts: T_c vs z for $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.7}\text{Y}_{0.3}(\text{Cu}_{1-z}\text{M}_z)_2\text{O}_{8+\delta}$ of (a) $M=\text{Co}$, (b) $M=\text{Zn}$ and various oxygen contents (measured for $z=0$): Δ as sintered $\delta \approx 0.33$, ∇ $\text{N}_2/350^\circ\text{C}$ annealed $\delta \approx 0.29$, \circ $\text{N}_2/500^\circ\text{C}$ annealed $\delta \approx 0.27$, \square quenched into liquid N_2 $\delta \approx 0.22$. The slope $|dT_c/dz|$ increases with decreasing δ . Lower charts: $T_c(z)/T_{c0}$ calculated from above data. Dotted lines are guides to the eye.

et al.,⁹ who investigated Ni- and Zn-substitution effects in optimum and oxygen deficient Y-123. Since Y-123 covers the underdoped regime, T_c drops with decreasing oxygen content and hence decreasing p . With decreasing p , T_{c0} decreases and the slope $|dT_c/dz|$ increases, leading to a decrease of \tilde{z}_c . In our samples with $x=0.3$ and $M=\text{Co}$, Zn , which are located in the underdoped regime, we observe the same behavior, as shown in Fig. 1.

In the case of $x=0$, the samples are located in the overdoped regime. With increasing δ , T_c decreases and the slope $|dT_c/dz|$ decreases as can be seen in the upper charts

of Fig. 2. In the lower charts of Fig. 2 we replotted our data as $T_c(z)/T_{c0}$, where $T_{c0} \equiv T_c(0)$. We find the data for samples with different δ and hence different p scaling on a single curve

$$T_c(p,z)/T_c(p,0) = g(z) \quad (3)$$

for each substituent M . Since $g(z)$ is independent of p , we can obtain \tilde{z}_c^M independent of δ and p as $\tilde{z}_c^{\text{Fe}} \approx 0.10$, $\tilde{z}_c^{\text{Co}} \approx 0.12$, $\tilde{z}_c^{\text{Ni}} \approx 0.21$, $\tilde{z}_c^{\text{Zn}} \approx 0.075$. Moreover, for overdoped samples the data replotted according to Eq. (3) allow for comparison with data of different authors, where the samples may differ in p due to deviations of the metal and oxygen stoichiometry. This can be seen from Fig 2, where we find Maeda's rescaled data in good agreement with our scaling curve.

Comparing \tilde{z}_c of $M=\text{Co}$ with that of $M=\text{Zn}$ in both regimes, we found that for samples with $x=0$ in the overdoped regime, $\tilde{z}_c^{\text{Co}} > \tilde{z}_c^{\text{Zn}}$, whereas for $x=0.3$ in the underdoped regime, $\tilde{z}_c^{\text{Co}} < \tilde{z}_c^{\text{Zn}}$. This is probably because substituting a trivalent ion like Co^{3+} (and Fe^{3+}) introduces an extra electron, which is not compensated by an increase of δ in the case of $x=0.3$. It leads to a decrease in p and hence to a reduction in \tilde{z}_c . This is consistent with the fact that we could not succeed in increasing δ of samples with $x=0.3$ by annealing in O_2 gas. On the other hand, in samples with $x=0$, which are easily oxidized, the extra electron due to a trivalent ion will be compensated by an increase of δ , but we concede that this compensation might be incomplete. Since this can lead to a slight change in the strengths of the effective T_c suppression also in the overdoped regime, we emphasize that Eq. (3) and the following discussion, strictly speaking, are only valid for divalent substituents. With due caution they may be applied also to trivalent substituents.

All the above findings indicate that $T_c(z)/T_{c0}$ and \tilde{z}_c do not depend on p in the overdoped regime, but are strongly p dependent in the underdoped regime. If this is a general behavior for all p -type high- T_c cuprates, it also should be observed in $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-z}\text{M}_z\text{O}_4$ (La-214), where it is possible to cover both regimes by substituting a corresponding

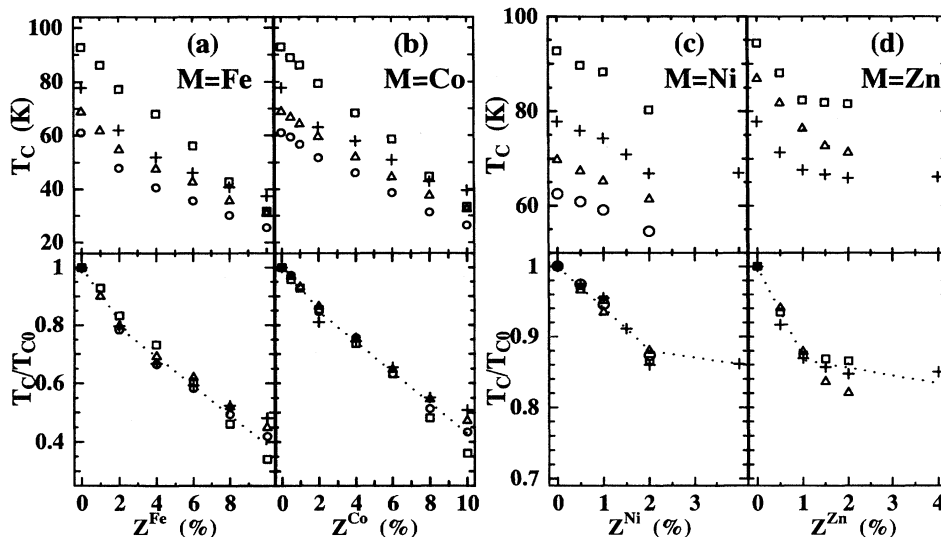


FIG. 2. (a)–(d) Upper charts: T_c vs z for $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{1-z}\text{M}_z)_2\text{O}_{8+\delta}$ of $M=\text{Fe}$, Co , Ni , Zn , respectively and various oxygen contents (measured for $z=0$): \square $\text{N}_2/600^\circ\text{C}$ annealed $\delta \approx 0.19$, Δ as sintered $\delta \approx 0.25$, \circ $\text{O}_2/600^\circ\text{C}$ annealed $\delta \approx 0.28$, $+$ data taken from Ref. 10. Lower charts: $T_c(z)/T_{c0}$ calculated from the above data. The dotted lines are guides to the eye, representing the scaling curves $g(z)$.

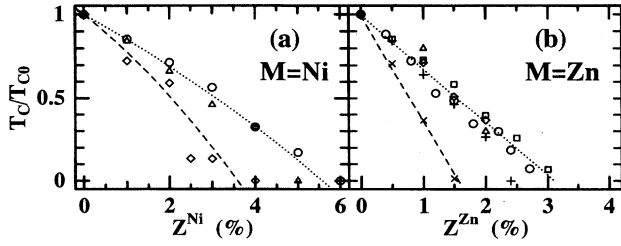


FIG. 3. Data taken from various publications on the $\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-z}\text{M}_2\text{O}_4$ system, replotted as $T_c(z)/T_{c0}$. (a) $M=\text{Ni}$: \diamond $x=0.10$, \triangle $x=0.15$, \circ $x=0.22$ (Ref. 6). (b) $M=\text{Zn}$: \times $x=0.10$, $+$ $x=0.15$, \square $x=0.20$ (Ref. 7); \circ $x=0.15$ (Ref. 12); \diamond $x=0.18$, \triangle $x=0.20$ (Ref. 8). All broken lines are guides to the eye, representing the scaling curves (dotted lines) in the overdoped regime ($x \geq 0.15$) and a deviating behavior (dashed lines) in the underdoped regime ($x = 0.10$).

amount of Sr^{2+} for La^{2+} . We therefore replotted data of various publications^{6–8,12} for $M=\text{Zn}, \text{Ni}$ as shown in Fig. 3. Here, p^{opt} corresponds to an optimal Sr concentration of $x^{\text{opt}} \approx 0.15$. Figure 3 confirms the scaling law in the overdoped regime ($x \geq x^{\text{opt}}$) and a breakdown of this behavior in the underdoped regime ($x < x^{\text{opt}}$).

From all the above results we now try to infer the implications on the experimental phase diagram as schematically shown in Fig. 4. For unsubstituted compounds ($z=0$), we adopt the parabolic behavior of $T_c(p,0) = f(p)T_{c0}^{\text{opt}}$ as proposed by Presland *et al.*⁴ With Cu-site substitution ($z > 0$), T_c is suppressed as given by $T_c(p,z) = g(z)T_c(p,0) = g(z)f(p)T_{c0}^{\text{opt}}$ with a p -independent factor $g(z) < 1$ in the overdoped regime. In the underdoped regime, the slope $|dT_c/dz|$ increases with decreasing p , and T_c therefore is suppressed stronger than $g(z)f(p)$, as indicated by the dot-

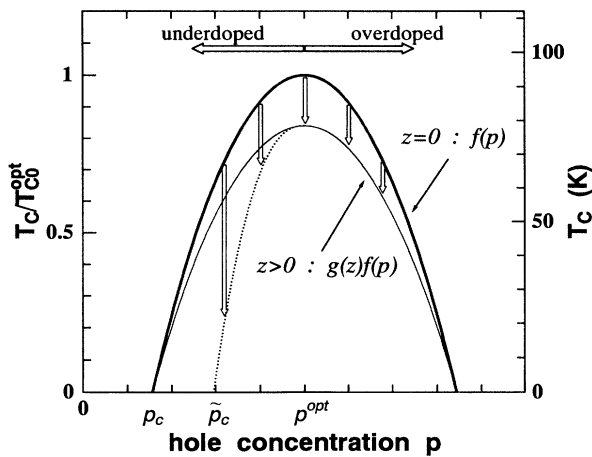


FIG. 4. Schematic p - T_c phase diagram of p -type high- T_c cuprates. For nonsubstituted samples, e.g., $z=0$, we adopted $T_c(p) = f(p)T_{c0}^{\text{opt}}$ as proposed in Ref. 4 (bold parabola). For substituted samples, e.g., $z > 0$, T_c is suppressed as indicated by the arrows. The right T_c scale corresponds to our Bi-2212 samples and the T_c suppression shown corresponds roughly to a substitution of $M=\text{Co}$ and $z=0.02$.

ted line. Hence p_c , the critical hole concentration for the appearance of superconductivity, shifts to a higher value \tilde{p}_c , as already observed in Y-123.¹³

The overdoped regime is often referred to exhibit Fermi-liquid properties. Therefore, we discuss our results in the framework of the Abrikosov-Gorkov (AG) pair-breaking theory.¹¹ According to AG, paramagnetic impurities cause pair breaking in s -wave superconductors with isotropic gap. In d -wave or extended s -wave superconductors with anisotropic gap, not only paramagnetic but also potential scatterers cause AG-like T_c suppression,^{14,15} given by

$$\ln\left(\frac{T_c}{T_{c0}}\right) = \chi \left[\psi\left(\frac{1}{2}\right) - \psi\left(\frac{1}{2} + \frac{\Gamma_N}{2\pi k_B T_c}\right) \right], \quad (4)$$

where Γ_N is the scattering rate in the normal state and $\chi \leq 1$ is related to the gap anisotropy.¹⁵ Linearizing the digamma function around $\psi(1/2)$ yields for small perturbations

$$\frac{T_c}{T_{c0}} = 1 - \chi \frac{\pi}{4} \frac{\Gamma_N}{k_B T_{c0}}. \quad (5)$$

Here, the term on the right-hand side depends on T_{c0} and therefore is dependent on p . This however is in contrast to our experimental results in the overdoped regime, where $T_c(z)/T_{c0}$ is independent of p . To reconcile Eq. (5) with our experimental result expressed as Eq. (3), we have to take into account the p dependence of Γ_N as well as that of T_{c0} .

In Born approximation or t -matrix approximation¹⁵ of the weak scattering limit (scattering phase shift $\delta_0 \rightarrow 0$), Γ_N is given by $\Gamma_N = \pi n_i N_0 u^2$, where $n_i \sim z$ is the impurity concentration, u characterizes the scattering potential, and N_0 is the p -dependent density of state (DOS) at the Fermi level ϵ_F . To recover our result, this requires $T_{c0} \propto N_0$ to cancel out the implicit N_0 dependence in Eq. (5). In the overdoped regime, T_{c0} decreases with increasing p and therefore N_0 would be required to decrease with increasing p .

In contrast, strong scattering in the unitarity limit (resonant scattering, $\delta_0 = \pi/2$) yields $\Gamma_N = n_i / \pi N_0$ in t -matrix approximation.^{15,16} In this case, to cancel out the N_0 dependence in Eq. (5), $T_{c0} \propto 1/N_0$ is required or, equivalently, the p independence of the product $T_{c0}N_0$ is required. Accordingly, N_0 has to increase with increasing p .

The p dependence of N_0 , however, is a very subtle issue in high- T_c cuprates, since ϵ_F and the DOS spectrum can change simultaneously with hole doping. According to measurements of the normal-state specific heat coefficient γ in the La-214 system,¹⁷ $N_0 \propto \gamma$ increases with increasing p in the whole superconducting range of p . As discussed above, such a p dependence of N_0 favors strong scattering rather than weak. Strong (resonant) scattering originally was discussed for heavy fermion systems and recently has been proposed also for high- T_c cuprates.^{15,16}

To be conclusive, however, it is necessary to verify the p independence of the product $T_{c0}N_0$ explicitly, which is necessary to explain pure resonant scattering for overdoped compounds in the above picture.

In summary, we have confirmed the current picture of two physically distinct regimes upon carrier doping by investigating the role of p on the T_c suppression by Cu-site substitution in Bi-2212. In the underdoped regime, the

T_c -suppression rate increases and \bar{z}_c decreases with decreasing p . Since p and \bar{z}_c are small, we expect localization effects to become important.¹⁸ In the overdoped regime, on the other hand, we found a scaling behavior of the T_c suppression, obeying the law $T_c(p,z)=g(z)T_c(p,0)$, with a p -independent scaling function $g(z)$, for all investigated substituents M =Fe, Co, Ni, and Zn. Comparison with systems as different as Y-123 and La-214 demonstrates the universality of this behavior among p -type high- T_c cuprates. It

can be understood qualitatively within the framework of an AG-like pair-breaking theory, provided that N_0 increases with increasing hole doping and strong scattering in the unitarity limit is taken into account.

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