Zn-induced T_c Reduction in High-T_c Superconductors: Scattering in the Presence of a Pseudogap

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The depression of T_c with fraction y of Zn substitution is studied across the underdoped and overdoped regions in La-214 and (Y,Ca)-123. The overdoped region is well described by elastic scattering at the unitarity limit with a d-wave strong-coupling superconducting order parameter. The underdoped region shows a marked increase in dT_c/dy, consistent with unitary scattering in the presence of an anisotropic normal-state pseudogap which depletes the density of states about E_F. [S0031-9007(97)04858-8]

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The effects of impurity substitution in high-T_c superconductors (HTS) fall into three categories: (i) altervalent substitutions in the noncopper sites which change the doping state, i.e., the hole concentration p; (ii) isovalent substitutions in the noncopper sites which have a remarkably small effect on superconducting properties; and (iii) substitution in the copper site which very rapidly depresses T_c. The last behavior is now qualitatively understood in terms of a d-wave order parameter which is strongly suppressed by isotropic elastic scattering in k space [1,2]. Much attention has focused on the marked difference in T_c reduction between Zn and Ni substitution in $YBa_2Cu_3O_{7-\delta}$ (Y-123). However, Y-123 appears to be anomalous in the case of Ni due to altervalent partial substitution on the chains. In the other HTS cuprates the effect of Ni substitution on T_c is much the same as that of Zn [3,4]. Recently, it has been noted that in underdoped cuprates there is a universal [5] and more rapid [3] suppression of T_c than on the overdoped side. Here, we advance a simple framework to understand this difference. The unitarity limit pair-breaking rate varies as the concentration y of scatterers and the inverse of the density of states (DOS) [2]. Beginning in the lightly overdoped region and extending back into the underdoped region, the normal-state pseudogap appears and grows, progressively depleting the DOS near E_F [6,7]. On the other hand, with the disappearance of the pseudogap in the more overdoped region, the DOS remains largely unchanged with doping [8]. As a consequence the rate of suppression, dT_c/dy, should remain constant on the overdoped side but climb rapidly with underdoping due to the appearance of the pseudogap. This is our first key point and we will see this is exactly what is found.

Our second point is that the quantitative description of these effects must build in the observation of *strong coupling* ($2\Delta_0/kT_c \approx 8$). We have previously shown [1] from μSR studies on La-214, Y-123, and (Y,Ca)-123 that the combined reduction in superfluid density and T_c by Zn substitution is consistent with unitary scattering with a d-wave order parameter. Nachumi *et al.* [9] in similar experiments claimed that while the *implicit* dependence of T_c on superfluid density agreed with the d-wave model [1] the *explicit* dependence of T_c on Zn content did not. We suggest that the discrepancy arises from the use of the *weak-coupling* d-wave model for which there is an unambiguous relation between the scattering strength and either T_c or Δ_0 [2]. Here we show for La-214 and (Y,Ca)-123 that the *explicit* dependence of T_c (and, by implication, the superfluid density [1]) on Zn content in the overdoped region is quantitatively consistent with unitary scattering within a *strong-coupling* d-wave scenario in which the critical Zn concentration is determined from Δ_∞ rather than T_{co}. A similar conclusion has been reported for La-214 by Mirza *et al.* [10]. Moreover, by assuming an anisotropic pseudogap as suggested by previous heat capacity [8,11], ARPES [12], and NMR [7] studies, and calculating the reduction in the normal-state DOS at T_c due to the pseudogap we are able to reproduce the T_c suppression as a function of p across the entire superconducting phase diagram for both (Y,Ca)-123 and La-214 *with no adjustable parameters.*

A series of samples of $Y_{0.8}Ca_{0.2}Ba_2Cu_{3-3y}Zn_{3y}O_{7-\delta}$ essentially free of Ca substitution on the Ba site were synthesized as described earlier [1]. Samples were annealed over a range of temperatures and oxygen partial pressures then quenched into liquid nitrogen to fix the oxygen deficiency δ. The thermoelectric power (TEP) was measured as a function of temperature and has been reported elsewhere [13]. The room-temperature TEP was used to determine the hole concentration [14] and, except for the most overdoped samples, was found to be independent of Zn concentration showing that Zn substitution does not alter the doping state [15]. $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ samples were synthesized by standard solid-state reaction at 1050 °C.

Figure 1(a) shows T_c plotted as a function of hole concentration ($p = x$) for $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ with $y =$ 0%, 1%, 2%, and 3%. For the (Y,Ca)-123 samples the primary data of T_c versus δ was shown in Fig. 1 of Ref. [1] and we plot T_c as a function of p for these samples in Fig. 1(b) for 0%, 2%, 4%, and 6% Zn substitution. The

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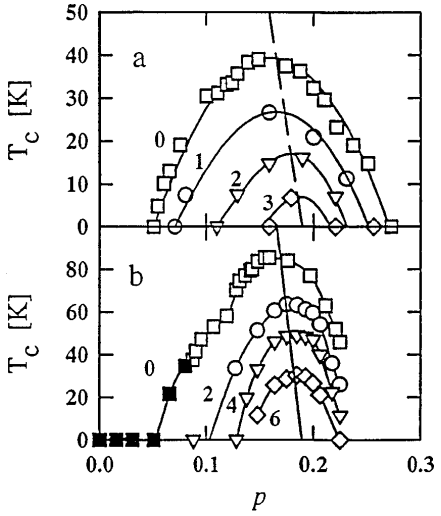

FIG. 1. T_c plotted as a function of hole concentration p for different values of Zn substitution annotated in %. (a) $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ and (b) $Y_{0.8}Ca_{0.2}Ba_2Cu_{3-3y}Zn_{3y}O_{7-\delta}$. Solid squares: $Y_{1-x}Ca_xBa_2Cu_3O_6$ where $p = x/2$.

sloping line falling to zero at $p = 0.19$ denotes the doping dependence of the pseudogap energy E_g, as determined for these samples from NMR [7] and from heat capacity [8], in both cases assuming an anisotropic pseudogap. It is notable that the phase curves for each Zn concentration do not collapse symmetrically about the optimal doping level for $y = 0$ as might be expected from pair breaking due to simple elastic scattering with a pair-breaking strength per Zn atom which is constant, independent of hole concentration. Rather, they are progressively displaced to higher hole concentration and appear to collapse about the descending pseudogap line. Similar behavior is seen in Fig. 1(a) for La-214 and here, in the absence of reliable data for $E_g(p)$ for this compound, we have used the same pseudogap line $E_g(p)$ from Fig. 1(b) rescaled by $T_{c,\max}$ and shown by the dashed line in Fig. 1(a). This is motivated by our previous observation [7] that E_g scales with $T_{c,\max}$ for a wide range of cuprates with $T_{c,\max}$ values ranging over a factor of 3 (La-214 at the low end, through La-2126 to Hg-1223 at the high end). The more rapid depression of T_c on the underdoped side together with the collapse about the pseudogap line is just what would be expected if the DOS at T_c were depressed due to the normal-state pseudogap as has been clearly demonstrated from both heat capacity [16] and NMR [7] studies. This problem, namely elastic scattering with a d-wave superconducting order parameter together with an anisotropic pseudogap (having three energy scales Γ, Δ_0, and E_g), does not appear to have been considered theoretically [17]. Here we present an approximate treatment which models the data remarkably well.

The T_c reduction for elastic scattering in weak-coupling d-wave superconductors follows the Abrikosov-Gorkov (A-G) equation [2]. This is subject to the condition, to be confirmed later, that the coherence length $\xi(T)$ suitably exceeds the mean spacing r_i between impurities. Thus

$$-\ln(T_c/T_{co}) = \psi[1/2 + \Gamma/(2\pi k_B T_c)] - \psi[1/2], \quad (1)$$

where $\psi[x]$ is the digamma function, $T_{co} = T_c(y = 0)$ and for unitary scattering $\Gamma = n_i/\pi g(E_F)$ is the pair-breaking scattering rate. Here $g(E_F)$ is the DOS per spin at the Fermi level and $n_i(=\alpha y_{ab}/abc)$ is the density of impurity scatterers with y_{ab} being the concentration of Zn atoms in the CuO_2 plane, α being the number of CuO_2 planes per unit cell and a, b, and c being the lattice parameters. For La-214 $\alpha = 1$ and $y_{ab} = y$ while, for Y-123, $\alpha = 2$, and $y_{ab} = 3y/2$. For *weak coupling* the critical scattering rate for suppression of superconductivity $\Gamma_c = 0.412\Delta_\infty = 0.88 k_B T_{co}$ but we note that many spectroscopies [8,16,18] indicate that HTS are in the *strong-coupling* regime with $2\Delta_0/k_B T_c \approx 8$. Should we therefore define Γ_c in terms of Δ_∞ or T_{co}? Our experimental observation is that the former is satisfied across the entire phase curve. Furthermore, we do find it plausible that the energy scale is set by Δ_∞ and not by T_{co} which, under strong-coupling corrections, is reduced due to pair breaking by *thermally excited* bosons. This mechanism is not likely to influence the critical concentration of impurities at which $T_c \to 0$ and thus the relation between Γ_c and Δ_∞ is probably unaffected by strong-coupling corrections. In the absence of a better theory we adopt $\Gamma_c = 0.412\Delta_\infty(=1.65 k_B T_{co})$ which provides a weaker suppression of T_c than in the weak-coupling case. Finally, the DOS may be determined from the temperature coefficient of the heat capacity $\gamma = C_V/T$ using:

$$\gamma = (2/3)\pi^2 k_B^2 g(E_F). \quad (2)$$

These relations are more clearly summarized in the linearized A-G equation for small Γ:

$$T_c/T_{co} = 1 - 0.69\Gamma/\Gamma_c = 1 - (29\alpha/\gamma\Delta_\infty)y_{ab}, \quad (3)$$

where γ is in units of $\mathrm{J/mol\,K^2}$. For a T- and p-independent DOS this means that the initial slope of the depression in T_c is constant, independent of doping p, and independent of T_{co}. In the overdoped region where the pseudogap is absent, the normal-state γ for $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ was found [8] to be constant with $\gamma = 1.9$ mJ/g atom $\mathrm{K^2} = (13 - \delta) \times 1.9\ \mathrm{mJ/mol\,K^2}$. Thus dT_c/dy_{ab} should at most vary only weakly with oxygen content in the overdoped region. Figure 2 shows T_c plotted as a function of Zn content for each of the oxygen (or hole) concentrations investigated. This shows a series of data curves $T_c(y)$ extending down from a value $T_{co} = T_c(y = 0)$ which, with increasing p, rises to a maximum $T_{co} = 85.5$ K at optimal doping then falls on the overdoped side. Filled symbols with solid lines denote overdoped samples, and open symbols with dashed curves denote underdoped samples. As expected, the overdoped region shows a series of curves progressively moving down in parallel. The solid curves, calculated from the A-G equation (1) fit the data rather well. On the other hand, beginning already with the optimally doped samples ($p = 0.16$) and extending into the underdoped region, the data $T_c(y)$ falls progressively more rapidly due to the

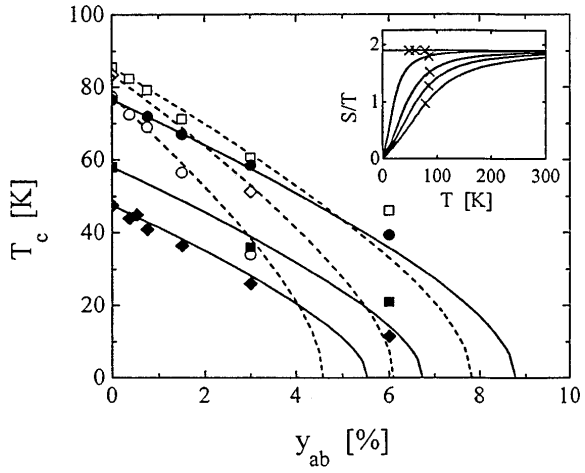

FIG. 2. Experimental and calculated (curves) values of T_c for $Y_{0.8}Ca_{0.2}Ba_2Cu_{3-3y}Zn_{3y}O_{7-\delta}$ plotted versus Zn concentration for different values of δ spanning from underdoped (open symbols, dashed curves) to overdoped (full symbols, solid curves). Values of p are 0.135 (○), 0.149 (◇), 0.16 (□), 0.196 (●), 0.217 (■), and 0.224 (◆). Inset: The temperature dependence of S/T in mJ/g atom K^2 where S is the electronic entropy calculated from Eq. (6) ignoring superconductivity. Curves are for (p, T_c, E_g) values of (0.135, 77.5, 285 K), (0.149, 83.5, 213 K), (0.16, 85.5, 156 K), (0.196, 76.5, 0 K), (0.217, 58, 0 K), and (0.224, 47.5, 0 K). Crosses mark values of S/T at T_c.

opening of the pseudogap. We return to this but first consider the validity of the A-G model which has been questioned recently by Franz *et al.* [19].

As noted by these authors A-G is self-consistent if $\xi(T) = \nu\xi_0(1 - T/T_{\rm co})^{-1/2}$ exceeds the mean spacing $r_i = a/\sqrt{y_{ab}}$ between impurities. Here ν is a constant of order unity (=0.74 for s-wave BCS). The bounding temperature T_b at which these lengths equate is given by

$$T_b/T_{\rm co} = 1 - y_{ab}(\nu\xi_0/a)^2. \quad (4)$$

We thus require that T_c should exceed T_b. Comparing with Eq. (3) we find

$$\xi_0/a > (5.41/\nu)[\alpha/\gamma\Delta_\infty]^{1/2} = 2.72/\nu\,, \quad (5)$$

for optimal Y-123 where $\Delta_\infty = 320$ K [8]. While this condition is just satisfied for Y-123 other HTS will meet it more easily. Moreover, in the overdoped region where $2\Delta_0/k_BT_c$ remains constant [8,18], ξ_0 diverges as T_c^{-1} ensuring increasing validity of A-G with overdoping.

Turning now to the effect of the pseudogap in the underdoped region, we use three approaches to estimate the changes to the A-G model. The pair-breaking strength is given by the ratio of the two energy scales Γ and Δ_∞. First, we vest the effect of the pseudogap entirely in Γ via the reduction in γ which we (a) calculate theoretically and (b) take from experimental data. Second, we take the alternative approach that, because the underlying DOS is constant, Γ is also constant and vest the effect of the pseudogap in Δ_0 via the pseudogap-suppressed order parameter. This is route (c). A more rigorous approach would treat Γ, Δ_0, and E_g all on an equal footing [17]. We consider each of these in turn.

(a) First, we note from NMR studies that while Zn substitution locally suppresses the pseudogap at nearest neighbors it does not affect the pseudogap more distantly until the Zn density is about twice the critical value for full suppression of superconductivity [15,20]. We thus assume E_g is independent of y. For $E_g(p)$ we use the solid linear curve shown in Fig. 1(b) and for the pseudogap we adopt a normal-state DOS with anisotropic gap $E_g(\mathbf{k}) = E_g|\cos(2\theta)|$ [7]. As an effective value of γ we take $\langle\gamma\rangle_{T_c} = S/T$ at T_c, since S/T is the average value of γ between 0 and T. The entropy S is determined from

$$S = -2k_B\int g(E)[f\ln f + (1-f)\ln(1-f)]\,dE\,, \quad (6)$$

where $f(E/kT)$ is the Fermi function. Values of $S(T)/T$ thus calculated are plotted in the inset to Fig. 2 for values of E_g corresponding to each doping level for the data shown in the main part of the figure. For each, $\langle\gamma\rangle_{T_c}$ shown by the crosses is read off and used to calculate the T_c reduction using Eq. (1). This is shown in Fig. 2 by the solid and dashed curves. Considering there are no adjusted parameters, the fit to the data is extremely good.

(b) Similar agreement is obtained by using the *experimental* values [8] of S/T which are reproduced in the inset to Fig. 3. These S/T curves confirm the constancy of the DOS on the overdoped side and its suppression on the underdoped side. The data in Fig. 2 are summarized in Fig. 3, which shows the experimental values for the initial slope $[dT_c/dy]_{y=0}$ plotted (filled circles) as a function of doping p, together with values calculated using our anisotropic pseudogap model (crosses) as well as using the experimental S/T values at T_c (diamonds). All values display the noted constancy in the overdoped side and the rapid rise on the underdoped side which begins with the opening of the pseudogap at $p = 0.19$. This provides strong confirmation of unitary scattering, for, in the Born limit $\Gamma \propto g(E_F)$ and dT_c/dy_{ab} would be expected to decrease with the opening of the pseudogap.

(c) Figure 3 shows the result of our third calculation (solid curve). Here we note that $\Gamma_c = 0.412\Delta_0$. If Δ_0 is reinterpreted as the low-temperature magnitude of the order parameter Δ_0', then this is reduced by the presence of the pseudogap. Following [16] and Bilbro and McMillan [21], when superconductivity and a normal-state gap compete for the same section of Fermi surface the quasiparticle excitations may be modeled by $E^2 = \varepsilon_k^2 + \Delta^2 = \varepsilon_k^2 + \Delta'^2 + E_g^2$ so that $\Delta_0'^2 = \Delta_0^2 - E_g^2$ where Δ is the total spectral gap. Thus $dT_c/dy_{ab} = 14.6/\gamma \approx 14.6/[1.9 \times 10^{-3}(13 - \delta)\sqrt{1 - (E_g/\Delta_0)^2}]$. As noted $\Delta_0 = 320$ K across the underdoped region [8]. Taking this and the p dependence of E_g shown in Fig. 1(b) we obtain the solid curve for dT_c/dy plotted in Fig. 3 which again agrees well with the experimental data.

Turning to $La_{2-x}Sr_xCuO_4$, Fig. 4 shows the Zn-induced T_c reduction for $x = 0.10$, 0.15, 0.20, and 0.22 taken from Ref. [3]. The same trend as seen for (Y,Ca)-123 is evident. The solid curves are again calculated from

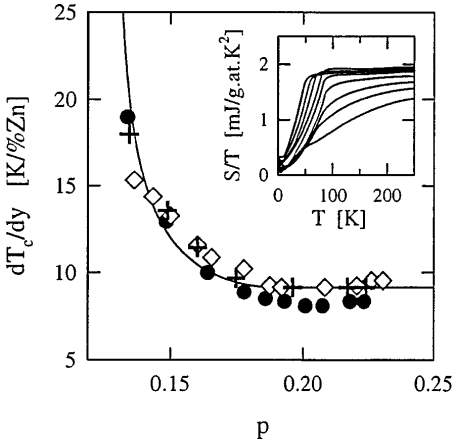

FIG. 3. The p dependence of dT_c/dy for $Y_{0.8}Ca_{0.2}Ba_2Cu_{3-3y}Zn_{3y}O_{7-\delta}$ extending from the under- to overdoped region. Experimental data: (solid circles); Calculated data: From theoretical S/T (crosses), from experimental S/T (diamonds), and from the order parameter model (solid curve). Inset: Experimental curves of S/T as a function of T from Ref. [8] for a range of δ values. T_c occurs at the points of discontinuous slope. (δ, T_c) values are $(0.04, 50.2)$, $(0.054, 54.4)$, $(0.125, 68.8)$, $(0.195, 79.9)$, $(0.247, 83)$, $(0.323, 85.5)$, $(0.439, 81.4)$, $(0.501, 70.2)$, and $(0.673, 48.8)$.

Eq. (1) using values of γ at T_c determined from the heat capacity [22]. The fit is very good except at the lowest doping level $p = 0.10$ where the rate of suppression is rather less than that predicted by the pseudogap model. We have noted previously [23] that for $p < 0.11$ there is evidence from μSR and NMR of electronic phase separation into hole-rich and hole-poor regions. We expect that the breakdown in the pseudogap model for dT_c/dz at $p = 0.10$ is associated with this.

Although an understanding of the nature of the pseudogap is still lacking, the above results point to a resolution of the long-standing debate concerning impurity substitution on the CuO_2 planes. There appear to be no additional intrinsic scattering terms (arising, for example, from the interactions giving rise to the pseudogap) that result in significant low-temperature pair breaking: $\gamma_0 = \gamma(T=0)$ is found to be very small or zero across the entire phase curve [8,11]. One clear implication is that there is a well-defined hole concentration, possibly the same in La-214 as in (Y,Ca)-123, at which the pseudogap opens, namely $p \approx 0.19$.

In summary, the depression of T_c with in-plane Zn substitution can be understood in terms of unitary scattering with a d-wave order parameter, combined, in the underdoped and lightly overdoped region, with the pseudogap-induced depression in the DOS. The pseudogap appears to close at a well-defined hole concentration $p \approx 0.19$ for both subject materials and almost certainly is the cause of the crossover between insulating and metallic states observed for $p < 0.18$ when $T \to 0$ [24].

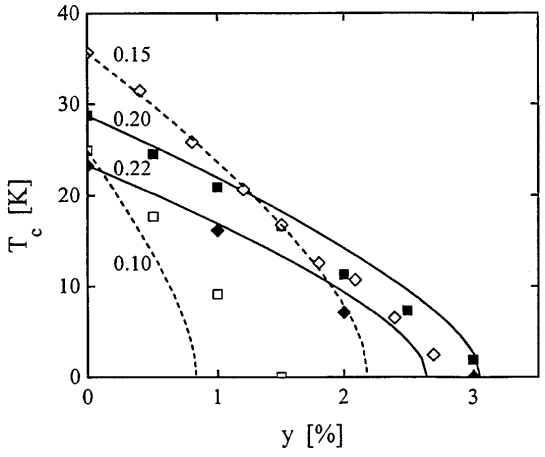

FIG. 4. Experimental and calculated (curves) values of T_c for $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ plotted as a function of Zn concentration for $p = 0.10$, 0.15, 0.20, and 0.22. Open symbols and dashed curves: underdoped. Solid symbols and full curves: overdoped.

[1] C. Bernhard *et al.*, Phys. Rev. Lett. **77**, 2304 (1996).
[2] Y. Sun and K. Maki, Phys. Rev. B **51**, 6059 (1995).
[3] T. Kluge *et al.*, Phys. Rev. B **52**, R727 (1995).
[4] R. Lal *et al.*, Phys. Rev. B **49**, 6382 (1994).
[5] Y. Fukuzumi *et al.*, Phys. Rev. Lett. **76**, 684 (1996).
[6] J. W. Loram *et al.*, Physica (Amsterdam) **235C–240C**, 134 (1994).
[7] G. V. M. Williams *et al.*, Phys. Rev. Lett. **78**, 721 (1997).
[8] J. W. Loram *et al.*, Physica (Amsterdam) **282C–287C**, 1405 (1997).
[9] B. Nachumi *et al.*, Phys. Rev. Lett. **77**, 2304 (1996).
[10] K. A. Mirza, J. W. Loram, and J. R. Cooper, Physica (Amsterdam) **282C–287C**, 1409 (1997).
[11] J. W. Loram *et al.*, *Advances in Superconductivity VII* (Springer-Verlag, Tokyo, 1995), p. 75.
[12] A. G. Loeser *et al.*, Science **273**, 325 (1996).
[13] C. Bernhard and J. L. Tallon, Phys. Rev. B **54**, 10 201 (1996).
[14] D. Obertelli, J. R. Cooper, and J. L. Tallon, Phys. Rev. B **46**, 14 928 (1992).
[15] G. V. M. Williams *et al.*, Phys. Rev. B **51**, 16 503 (1995).
[16] J. W. Loram *et al.*, J. Supercond. **7**, 243 (1994).
[17] Since completing this work we have carried out the full calculation: G. V. M. Williams, E. M. Haines, and J. L. Tallon, Phys. Rev. B (to be published).
[18] C. Kendziora and A. Rosenberg, Phys. Rev. B **52**, R9867 (1995); M. Kang *et al.*, Phys. Rev. Lett. **77**, 4434 (1996).
[19] M. Franz *et al.*, Phys. Rev. B **56**, 7882 (1997).
[20] A. V. Mahajan *et al.*, Phys. Rev. Lett. **72**, 3100 (1994).
[21] G. Bilbro and W. L. McMillan, Phys. Rev. B **14**, 1887 (1976).
[22] J. W. Loram *et al.*, in *Proceedings of the 10th Anniversary HTS Workshop* (World Scientific, Singapore, 1996), p. 341.
[23] J. L. Tallon *et al.*, Physica (Amsterdam) **282C–287C**, 236 (1997).
[24] G. S. Boebinger *et al.*, Phys. Rev. Lett. **77**, 5417 (1996).