Universal T_c suppression by in-plane defects in high-temperature superconductors: Implications for pairing symmetry

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The influence of in-plane oxygen defects on the critical temperature, resistivity, and Hall coefficient was studied in $YBa_2Cu_3O_{6+x}$ (YBCO) films with different oxygen contents (T_{c0} ranging from 30 to 93 K) with emphasis on the underdoped ''spin-gap phase.'' A strong T_c suppression was observed, but no influence of the defects on ''spin-gap'' features in the transport properties was found. A comparison is made with T_c suppression by other in-plane defects such as Zn substitutions for Cu, Pr substitutions for Y in YBCO, and radiation defects in Bi-2201 and Bi-2212 high-T_c superconductors. T_c suppression by defects is shown to occur in a universal way which is independent of the T_{c0}, carrier concentration, and number of CuO_2 planes per unit cell. It is shown that, independent of whether the in-plane defects induce localized magnetic moments or not, T_c is a universal function of the impurity scattering rate, which can be described by the pair-breaking theory for potential scatterers in d-wave superconductors, but requires that the pair-breaking rate be a factor of 3 smaller than that suggested by the transport data. An alternative description of the T_c suppression in terms of the phase fluctuation theory proposed recently by Emery and Kivelson is also discussed. [S0163-1829(96)02618-5]

I. INTRODUCTION

The symmetry of the order parameter in high-temperature superconductors (HTS's) is being actively studied and debated. While there have been a number of experiments suggesting an anisotropic pairing in HTS's, the issue of whether it is d-wave (DW) or anisotropic s-wave (ASW) has not yet been settled.[1] T_c suppression by defects provides one venue of study: Nonmagnetic defects act as pair breakers in anisotropic pairing superconductors[2–5] (APS's), while they have little effect on T_c in isotropic s-wave (ISW) superconductors,[6] provided that disorder does not change the density of states, $N(0)$. DW's can be further distinguished from ASW's due to a qualitatively different dependence of T_c on the impurity scattering rate.[4,5] Since the carrier transport and superconducting pairing are believed to be confined to two-dimensional (2D) CuO_2 planes, of main interest are in-plane defects on both Cu and O sublattices such as substitutions for Cu, Cu vacancies and interstitials, and in-plane oxygen vacancies and interstitials. The drawback of defect-induced T_c suppression as a test for pairing symmetry is the unfortunate fact that the magnetic state of in-plane defects is not precisely known—magnetic defects suppress T_c at any symmetry of singlet pairing.[7]

The only practical way to produce in-plane oxygen defects in a controllable manner is to use electron irradiation.[8–12] By studying in a wide range the changes in T_c and resistivity induced by in-plane O defects in optimally doped $YBa_2Cu_3O_{6.9}$, we have shown that T_c suppression is qualitatively consistent with d-wave pairing symmetry.[11] We have found, however, that quantitative agreement with pair-breaking theory for d-wave superconductors can only be achieved if the pair-breaking scattering rate is a factor of 3 smaller than the impurity scattering rate deduced from the observed defect-induced resistivity.

In this work we present the data on the effect of in-plane oxygen defects on resistivity, Hall coefficient, and critical temperature in underdoped $YBa_2Cu_3O_{6+x}$ (YBCO) thin films with x in the range from 0.5 to 0.7 corresponding to the initial critical temperatures T_{c0} from ~30 to ~60 K. At these dopings, the development of a pseudogap and/or spin gap is clearly observed in optical, NMR, and neutron scattering experiments, and the transport properties are believed to be governed by this gap opening.[13] So the influence of in-plane oxygen defects on both T_c and spin-gap phenomena can be studied. Analyzing a set of transport data on HTS's with T_{c0} ranging from 93 to 10 K, we have found that T_c suppression by in-plane defects induced by irradiation is a universal function of the impurity scattering rate, independent of T_{c0}, carrier concentration, and the number of CuO_2 layers in the unit cell. We present an analysis of the results in terms of pair-breaking theory for d-wave superconductors, assuming nonmagnetic character of in-plane defects, and for s-wave superconductors, assuming the existence of localized magnetic moment associated with defects. We show that the data favor d-wave pairing symmetry and discuss how the pair-breaking parameters in either case are constrained by the transport data. As an alternative explanation, we consider T_c suppression by phase fluctuations as proposed recently by Emery and Kivelson.

II. EXPERIMENT

The films used in this study were epitaxially grown on $LaAlO_3$ substrates by the BaF_2 method using post-annealing (780 °C in wet O_2+N_2 mixture at $p_{O_2}=300$ mtorr) with subsequent oxidation (30 min at 500 °C in 1 atm of O_2) followed by slow cooling. The fabrication details, microstructure, and

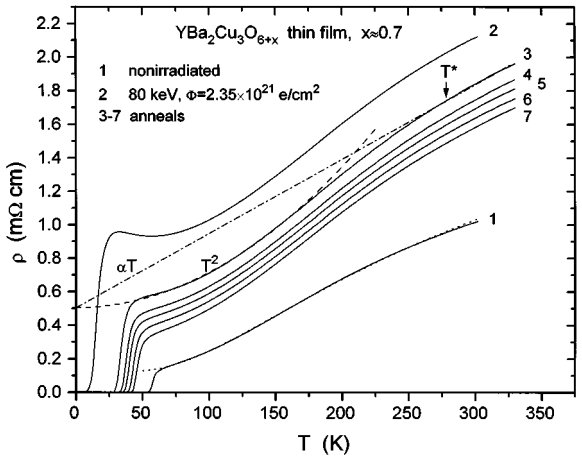

FIG. 1. Temperature dependences of the in-plane resistivity of $YBa_2Cu_3O_{6+x}$ thin film with $x \approx 0.7$ (sample No. TY-41). Curve (1), nonirradiated, $T_{c0} = 57.4$ K; curve (2), after 80-keV electron irradiation with the dose $2.35 \times 10^{21} e/\mathrm{cm}^2$ inducing ~ 0.12 in-plane O vacancies per unit cell, $T_c = 15.3$ K; curves (3)–(7) correspond to anneals at 330 K in He for 0.5, 1, 1.5, 2.5, and 5 h, respectively. The dashed curve shows the T^2 fit and suggested residual resistivity ρ_0; dash-dotted curves show the T-linear fit, slope α, to the high-temperature region. The dotted curve is the fit by a $\exp(-\Delta/T)$ dependence; see text.

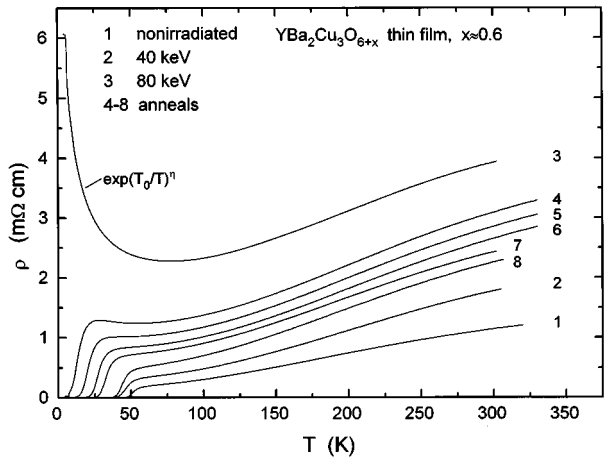

FIG. 2. Temperature dependences of in-plane resistivity of $YBa_2Cu_3O_{6+x}$ thin film with $x \approx 0.6$ (sample No. TY-38). Curve (1), nonirradiated, $T_{c0} = 51.4$ K; curve (2), after electron irradiation with the energy $E = 40$ keV, which is below the threshold for plane oxygen displacement, $\Phi = 1.8 \times 10^{21} e/\mathrm{cm}^2$, $T_c = 47$ K; curve (3), after 80-keV electron irradiation with the dose $2.13 \times 10^{21} e/\mathrm{cm}^2$ inducing ~ 0.12 in-plane O vacancies per unit cell, $T_c < 3$ K if it even exists; curves (4)–(6) correspond to anneals at 330 K in He for 0.5, 1, and 2 h, respectively; curves (7) and (8) correspond to additional anneals for 60 h and 8 months at room temperature, respectively.

properties of the films are given elsewhere.[14] The samples presented lithographically defined six probe patterns with a 10-μm-wide and 40-μm-long current channel. The film thickness was 50 nm. The samples were annealed at 200 °C in He flow to reduce the oxygen content, which was estimated by comparing the T_c, resistivity, and Hall coefficient with literature data on deoxygenated films grown by the BaF_2 method, by laser ablation, and with the data on bulk samples. The data on five samples have been collected and found to be reproducible. The typical results are given below. In-plane oxygen defects (vacancies) were induced by 80-keV electron irradiation at room temperature. Details of the irradiation procedure, the evaluation of oxygen displacement energy, and a discussion of the defect formation mechanism and kinetics, as well as some of the defect characteristics can be found in Ref. 11.

Figures 1 and 2 show the typical resistivity data for two samples (Nos. TY-41 and TY-38, respectively). After initial characterization both samples were irradiated to induce in-plane O vacancies, characterized again, and then annealed at 330 K in the He atmosphere of the cryostat. Annealing was interrupted by the transport measurements. The concentrations of induced in-plane vacancies, N_v, were estimated, respectively, as 0.122 and 0.118 cell^{-1} for TY-41 and TY-38, using the oxygen displacement energy 8.4 eV, displacement cross section $\sigma_d = 6.09 \times 10^{-23}$ cm^2, and spontaneous recombination volume of 21 unit cells, evaluated in Refs. 10 and 11. Induced Frenkel pairs (in-plane O vacancy + an interstitial which is thought to be far from the planes) recombine at annealing. So the concentration of in-plane vacancies can be reduced virtually to zero in such a way that neither the oxygen content nor the microstructure of the samples can change. This is a unique possibility which is extremely difficult to realize when in-plane defects are produced by chemical substitution. It is seen that the critical temperature, resistivity, and Hall coefficient recover at annealing, asymptotically approaching their values in the nonirradiated sample; complete recovery, strictly speaking, requires an infinitely long annealing time because of a stretched exponential annealing kinetics.

Two important features of the ρ-vs-T dependences have to be mentioned. First, the $\rho(T)$ curves have a pronounced downturn (S shape) below the temperature T^* above which the $\rho(T)$ curves are nearly linear. This downturn is believed to arise due to the opening of the spin gap below T^* which leads to the freezing off of spin fluctuation scattering.[13] Optical and resistivity data indicate the development of a pseudogap below T^* for the transport in the c direction.[15,13] Second, the $\rho(T)$ curves after anneals are perfectly parallel and can be obtained from each other by a shift along the ρ axis, corresponding to the change in defect-induced residual resistivity, i.e., $\rho = \rho_0 + \rho_1(T)$, which indicates that the T-dependent (inelastic) scattering and impurity scattering are additive. The degree to which the T-dependent part $\rho_1(T)$ remains unchanged is much higher than that observed in Zn-doped YBCO single crystals.[16,17] If we accept that the T-dependent part is due to spin fluctuation scattering, the data presented indicate that *in-plane oxygen defects do not change the spectrum of spin fluctuation and have no influence on the spin (pseudo) gap*. Indirectly, this also suggests that in-plane oxygen defects are nonmagnetic.

In the temperature range from T_c up to some 150 K, $\rho(T)$ can be described as $\rho_0 + aT^n$ with n in the range from 1.9 to 2.1, as shown in Fig. 1. This is in agreement with previous observations.[13] Note, however, that in a much wider temperature range from slightly above T_c up to T^*, the $\rho(T)$ can be described by $\rho_0' + b \exp(-\Delta/T)$ with a *temperature-independent* parameter Δ. As an example, one such fit is

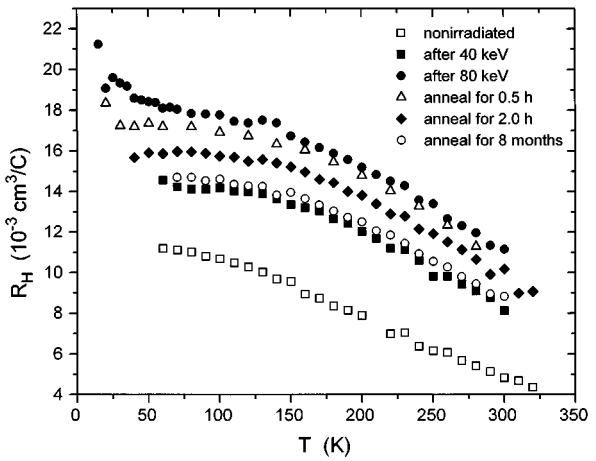

FIG. 3. Hall coefficient for the sample No. TY-38. Curve (□), nonirradiated; curves (■), (●), after 40-keV and then 80-keV electron irradiations, same doses as in Fig. 2; curves (△), (◆), annealed in He at 330 K for 0.5 and 2 h, respectively; curve (○), after an additional anneal for 8 months at room temperature.

shown in Fig. 1 for the nonirradiated sample; it gives $\rho_0'=0.124$ mΩ cm, $b=2.45$ mΩ cm, and $\Delta=298$ K. We have checked that this dependence also fits the published resistivity data on underdoped YBCO.[13,18] The residual resistivities ρ_0' suggested by these fits are ~20% higher than the residual resistivities ρ_0 which follow from the power-law fits. Parameter Δ increases with decreasing doping, and its value agrees surprisingly well with the temperature T^* above which the ρ-vs-T curves display a T-linear dependence. It is worth mentioning that the same T dependence was found to fit the resistivity data on $A15$ superconductors in the extremely wide range of T.[19]

If superconductivity is suppressed by the irradiation, the $\rho(T)$ curves display an upturn at low temperatures and follow a variable-range-hopping (VRH) temperature dependence $\rho=\rho_c\exp(-T_0/T)^{\eta}$. The fit to the data shown in Fig. 2, curve 3, gives $\rho_c=613$ μΩ cm, $T_0=179$ K, and $\eta=0.233$, which is very close to Mott's $\eta=1/4$ for VRH in 3D systems. The signs of localization at low T appear when the residual resistivity exceeds ~0.6 mΩ cm. However, the temperature dependence of ρ at high temperatures remains the same as in a low-residual-resistivity state even if strong localization takes place at low T (compare, e.g., curves 3 and 2 in Fig. 2). In a picture of propagating quasiparticles, this could only be understood if at high temperatures $k_F l\gg 1$ in the entire range of defect concentrations; here, l is the mean free path. If so, localization at low T should be viewed as arising due to diminishing inelastic scattering.

The Hall coefficient data for TY-38 are shown in Fig. 3. The sample was first irradiated with 40-keV electrons and then with 80-keV electrons. The former energy is below the threshold for in-plane O displacement, while the latter is above.[11] It is seen that there is an increase in the Hall coefficient after each irradiation, suggesting a possible change in carrier concentration p. The increase in R_H after 40-keV irradiation correlates with the overall increase in the resistivity slope (see curve 1 and curve 2 in Fig. 2). A reduction of carrier concentration could be due to the disordering, or possibly some loss, of oxygen in the basal plane (in ''chains''), which occurs simultaneously with the production of in-plane O defects, but is characterized by a different displacement energy.[11] However, the change in T_c due to a chain disorder effect on p is much smaller than the change due to in-plane defects, as follows from the comparison of shifts in T_c and R_H induced by equal amounts of electron irradiation with the energy below and above the threshold. Also, the changes in R_H induced by in-plane O defects are reversible; the Hall coefficient decreases at annealing and asymptotically approaches the R_H before irradiation, while its temperature dependence remains unchanged as well as the slopes of the resistivity curves. The changes induced by the 40-keV irradiation do not appear to be possible to anneal at the annealing temperatures used.

The changes in R_H induced by in-plane O defects are equivalent to those observed at Zn substitution for Cu.[17,16] So it appears that R_H always increases with increasing in-plane scattering. It was argued that there is no simple and direct relation between the R_H and carrier concentration in HTS's and, therefore, the increase in R_H induced by in-plane defects is a result of an interplay between different scattering processes rather than a decrease in carrier concentration.[17,16]

III. DISCUSSION

A. Pair breaking

We now turn to the defect-induced T_c suppression. An explanation based on lifetime broadening effects, widely invoked in transition-metal superconductors, can be ruled out, an issue which lies beyond the scope of this paper. We consider the depairing mechanism which was found to provide a qualitative description of radiation-induced T_c shifts in various HTS's.[20] The issue whether the in-plane oxygen defects are nonmagnetic or magnetic has yet to be resolved. We have presented above some arguments in support of the nonmagnetic nature of these defects. Some evidence also comes from the susceptibility data (for a discussion, see Ref. 9). On the other hand, screening the positive charge of the O vacancy requires expelling the holes from the region surrounding the defect, which could lead to the formation of a magnetic moment on neighboring Cu atoms. Although these seem unlikely to behave as free moments due to a strong interaction, for completeness, we consider both nonmagnetic and ''magnetic'' vacancies, giving alternatives in square brackets.

T_c in APS's [ISW's] with nonmagnetic [magnetic] defects is given by[2,4,7]

$$\ln\frac{T_{c0}}{T_c}=\chi\left\{\psi\left(\frac{1}{2}+\frac{1}{4\pi\tau T_c}\right)-\psi\left(\frac{1}{2}\right)\right\}, \tag{1}$$

where ψ is the digamma function, χ is a measure of the order parameter anisotropy, and T_{c0} is the critical temperature in the defect-free material. In APS's with nonmagnetic defects [ISW's with magnetic defects], the pair-breaking lifetime τ corresponds to the impurity potential scattering lifetime τ_p [spin-flip scattering lifetime $\tau_s/2$]. Both scattering lifetimes can be expressed in terms of the concentration of defects and corresponding scattering potentials. For instance, in the Born approximation the well-known expressions are[7,21]

$$1/\tau_p=2\pi N(0)n_d V^2, \tag{2a}$$

$$1/\tau_s = 2\pi N(0) n_d J^2 S(S+1)/4, \tag{2b}$$

where V and J are the potential and exchange parts of the impurity potential, respectively, S is the impurity spin, and n_d is the concentration of impurities. If $\chi=1$, T_c drops to zero at a critical scattering rate $1/\tau_{pc}=1.76T_{c0}$ $[1/\tau_{sc}=0.88T_{c0}]$.

Let us assume first that the in-plane oxygen defects are nonmagnetic. The data presented here and in our previous work[11] as well as in Ref. 20 indicate that T_c is completely suppressed at a finite and fairly low concentration of defects, indicating that χ is close to 1. This also suggests that the pairing symmetry is not an ASW; otherwise, T_c, after initial reduction, would saturate at a nonzero value.[4] So we set $\chi=1$ and consider d-wave pairing. None of the impurity scattering parameters are known, however, and the determination of exact in-plane defect concentrations is also complex (not only in irradiation, but also in substitution experiments). Therefore, the only way to make a comparison with the theory is to use the defect-induced resistivity as a measure of the contribution of all the defects retained in a sample up to T_c measurements and to use the transport impurity lifetime $\tau_{\rm imp}$ instead of quasiparticle lifetime τ_p. Then the pair-breaking rate can be expressed in terms of ρ_0,

$$1/\tau_{\rm imp} = \rho_0 \omega_p^2/4\pi, \tag{3}$$

where ω_p is the plasma frequency, which, in general, may be renormalized due to strong-coupling effects.[3] Since we want to analyze the T_c suppression in YBCO samples with different carrier concentrations, in irradiated $Bi_2Sr_2CaCu_2O_8$ (2212) and $Bi_2Sr_2CuO_6$ (2201) single crystals[12] and in Zn-doped YBCO single crystals,[16,17] this would require knowledge of ω_p or carrier concentrations in all of these materials. While there have been a number of measurements of ω_p in YBCO and other HTS's, determination of ω_p from the optical data is not straightforward, and the reported values gradually reduce in the course of time. Yet another problem is how to make an accurate comparison of the resistivity data on samples with different microstructures and quality such as single crystals and thin films. We have shown earlier that a convenient representation of impurity scattering is provided by the quantity ρ_0/α, where α is the slope of the T-linear resistivity, since the major sources of errors in determination of $\tau_{\rm imp}$ cancel in this ratio.[11] In the T-linear resistivity region, the transport scattering rate is $1/\tau_{\rm imp}+2\pi\lambda T$, where λ is the electron-boson transport coupling constant. Hence $1/\tau_{\rm imp}=2\pi\lambda\rho_0/\alpha$. Since we want to relate the change in T_c with the defect-induced change in scattering, the parameter of interest is $(\rho_0/\alpha-\rho_{00}/\alpha_0)$, where ρ_{00} and α_0 are, respectively, the residual resistivity and T-linear resistivity slopes in the nonirradiated (or unsubstituted) sample. Correspondingly, T_{c0} should be taken as its critical temperature. Throughout this paper, we will use the midpoint of resistive transitions to define the T_c.

The determination of α from the resistivity data[9,11,12] on irradiated samples of optimally doped YBCO, Bi-2212, and Bi-2201 with T-linear resistivities is straightforward; ρ_0 is the extrapolation of a linear fit to $T=0$. Note that generally α is not constant, but increases somewhat with the concentration of in-plane defects. In oxygen-deficient YBCO, the $\rho(T)$ curves are known to become linear at $T>T^*$.[13,18] In oxygen-deficient Zn-doped YBCO, the $\rho(T)$ are also linear at $T>T^*$.[16] Therefore, we suggest the use of the slopes taken in this high-T region, despite their higher uncertainty in the O-deficient samples than in the optimally doped ones. At high temperatures, the data were fitted to $\rho(T)=\rho_0+\alpha T$ and ρ_0 was constrained so as to be close to the value which follows from the power-law fit in the $T<T^*$ region. The data on irradiated fully oxygenated films[11] display a short plateau in T_c at low irradiation doses, apparently due to a superposition of the effects of chain and plane defects. For these data, the value of ρ_{00}/α_0 was taken as that which corresponds to the end of this plateau and above which T_c starts to decrease. The typical values of ρ_{00}/α_0 are 33 and 40 K in $x=0.9$ and 0.7 samples, respectively.

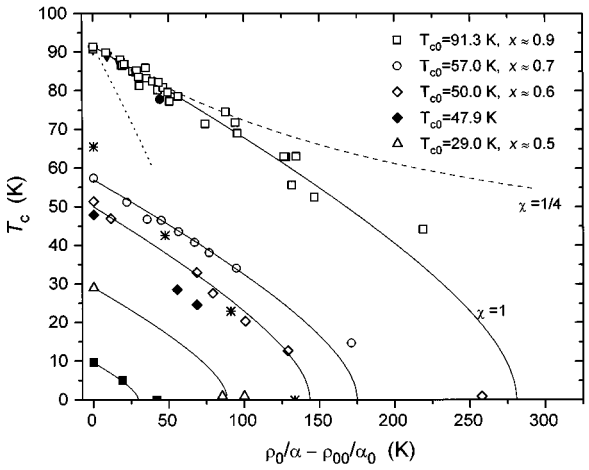

FIG. 4. Critical temperature of $YBa_2Cu_3O_{6+x}$ with in-plane oxygen defects vs the normalized residual resistivity $(\rho_0/\alpha-\rho_{00}/\alpha_0)=1/2\pi\lambda\tau_{\rm imp}$. The data for $x\approx0.9$ thin films were obtained in our previous work (Ref. 11). Also shown are the data on a 350-keV electron-irradiated YBCO single crystal (▼), 2.5-MeV electron-irradiated Bi-2212 (●) and Bi-2201 (■), and $YBa_2Cu_{3-z}Zn_zO_{6.63}$ ($z=0$, 0.03, 0.06, and 0.09) single crystals (∗), inferred from Refs. 9, 12, and 16, respectively. Solid lines are the best fits to the pair-breaking theory, corresponding to either a DW superconductor with nonmagnetic impurities [Eq. (1)+Eq. (4) at $\lambda=0.092$] or an ISW superconductor with magnetic defects [Eq. (1)+Eq. (5) at $\lambda=0.3$ and $\beta=0.18$]. The dotted line is the prediction of conventional pair-breaking theory for a $d_{x^2-y^2}$-wave superconductor at $\omega_p=1.1$ eV ($\lambda=0.3$). The dashed curve is the best fit to ASW with the same nodal structure $\chi=1/4$ [Fehrenbacher and Norman (Ref. 5)].

In Figs. 4 and 5 we have plotted T_c in the irradiated YBCO films with different oxygen contents as a function of $(\rho_0/\alpha-\rho_{00}/\alpha_0)$ and also included the data on irradiated $YBa_2Cu_3O_{6.9}$, Bi-2212, and Bi-2201 single crystals extracted from Refs. 7 and 12, and on $YBa_2Cu_{3-z}Zn_zO_{6+x}$ ($x=0.93$ and 0.63) extracted from Refs. 17 and 16. Being presented in this way, T_c suppression data in the irradiated HTS's are alike (curves are parallel). This suggests that T_c suppression by in-plane radiation defects has a universal character which is *independent of carrier concentration and* T_{c0}, independent of the number of CuO_2 planes in the unit cell, and whether the HTS is in the form of a film or single crystal. It is also independent of whether the in-plane defects are oxygen va-

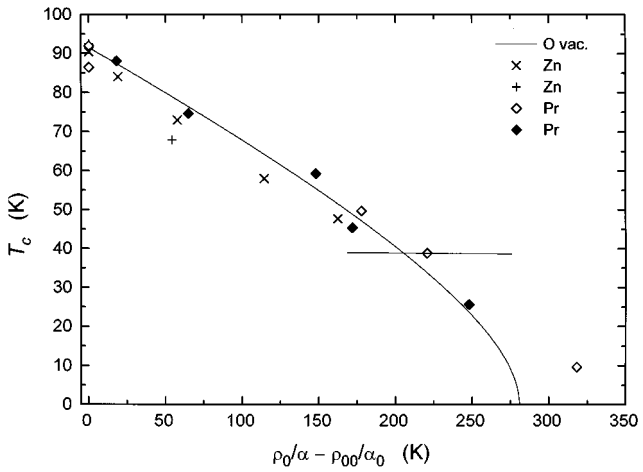

FIG. 5. Critical temperature of $YBa_2Cu_{3-z}Zn_zO_{7-\delta}$ and $Y_{1-y}Pr_yBa_2Cu_3O_{7-\delta}$ vs the normalized residual resistivity. The data were inferred from Ref. 17 (×), Ref. 16 (+), Ref. 28 (♦), and Ref. 29 (◇). The error bar shown applies only for this particular data point. The solid line is the best fit by pair-breaking theory for the thin-film samples with in-plane oxygen defects (same curve as in Fig. 4).

cancies as in our low-energy electron irradiations or both oxygen and copper vacancies as in high-energy irradiation experiments.[9,12]

It is important to note that T_c suppression per in-plane O vacancy $\delta T_c \equiv (T_{c0}-T_c)/N_v$ in YBCO increases with decreasing carrier concentration from about 280 K per defect in the unit cell in $x=0.9$ samples[11] to ~350 K in $x=0.7$ and ~650 K in $x=0.6$ samples. In Zn-doped samples, $\delta T_c \equiv (T_{c0}-T_c)/z$ also increases from ~400 to ~700 K with x decreasing from 0.93 to 0.63.[16,17] Since $\delta T_c \propto N(0)V^2$ according to Eqs. (1) and (2), the increase in δT_c implies that V should also increase with decreasing carrier concentration, which seems reasonable because screening the charge of defects becomes less effective. The estimates of V were given in Refs. 11, 20, and 23. Also, as follows from the data in Ref. 12, the δT_c due to in-plane defects in a single-layered Bi-2201 ($T_{c0} \approx 10$ K) is roughly 1.6 times less than in bilayered Bi-2212 ($T_{c0} \approx 90$ K). This is consistent with the pair-breaking mechanism because $N(0)$ in a single-layered HTS's should be a factor of 2 smaller than in a bilayered one. Note that the above data contradict the claim made in Ref. 20 that T_c suppression in different HTS's can be described using the same parameter $N(0)V$ for different materials. However, we find that all the data can indeed be scaled on the universal curve T_c/T_{c0}-vs-normalized scattering rate τ_{cr}/τ_{imp}. The fits which are discussed below suggest $\tau_{cr}^{-1} \approx 3.07 T_{c0}(2\pi\lambda)$.

The experimental data were fitted by Eq. (1) with

$$1/\tau_p = 1/\tau_{imp} = 2\pi\lambda(\rho_0/\alpha - \rho_{00}/\alpha_0), \tag{4}$$

as shown in Fig. 4. The only fitting parameter is λ, which was found to be 0.092(4) for all the HTS samples analyzed. This value is a factor of 3 smaller than the usually accepted value $\lambda=0.3$, which, in optimally doped YBCO, was estimated from the absence of resistivity saturation at high temperatures[22] and which follows from the observed α and optical plasma frequency $\omega_p=1.1$ eV. Similarly, if we use the bare change in ρ_0 corresponding to the vertical shift of $\rho(T)$ curves in Figs. 1 and 2 and Eq. (3) for the pair-breaking rate, the fits suggest the renormalized plasma frequency to be $\omega_p^*=0.61$ and 0.39 eV in $x=0.9$ and 0.7 samples, respectively. These plasma frequencies imply a mass enhancement m^*/m, correspondingly, ~7 and ~10 if we use the carrier concentration which follows from the bond valence sums,[24] respectively, $p=0.17$ and 0.1 holes per CuO_2 plane for $x=0.9$ and 0.7 samples. It is worth mentioning that m^*/m increases roughly as $1/p$. For a comparison, the optical data suggests $\omega_p=1.1-1.4$ eV for $x=0.9$ and $\omega_p=0.75-0.9$ eV for $x=0.7$.[25,26] So either the HTS's can withstand a considerably stronger impurity scattering than that allowed by conventional pair-breaking theory for d-wave superconductors or the *actual pair-breaking rate in HTS's is a factor of 3 smaller than the transport impurity scattering rate*. The possible sources of this reduction are strong-coupling effects and/or scattering anisotropy.[2,3] If scattering is anisotropic, the $1/\tau_p$ in Eq. (1) should be multiplied by $(1-g_I)$, where g_I is the scattering anisotropy[2] and $-1 \leqslant g_I \leqslant 1$. While, in general, one expects $|g_I| \ll 1$, the fit to the data would require g_I to be 0.67 if $\lambda=0.3$ (or $\omega_p=1.1$ eV) were used. The strong-coupling correction should also be small since we use the experimental (already renormalized) plasma frequency.[3] The estimates presented in Ref. 11 indicate that the scattering off in-plane oxygen defects should involve s, p, and d channels, and so a combination of modest scattering anisotropy and strong coupling could be a plausible resolution.

Let us consider next the possibility that in-plane oxygen vacancies are magnetic. Then, if pairing symmetry is d wave, an admixture of spin-flip scattering to the potential scattering would only increase the pair-breaking rate $1/\tau = 1/\tau_p + 2/\tau_s$ and thus cannot explain the observed difference between the transport scattering rate and the pair-breaking rate required to fit the data. If the symmetry is s wave, only the spin-flip events are pair breaking. For the impurity scattering we can write $1/\tau_{imp} = 1/\tau_p + 1/\tau_s$ and express $1/\tau_s$ in terms of the resistivity characteristics

$$1/\tau_s = 2\pi\lambda(\rho_0/\alpha - \rho_{00}/\alpha_0)\,\frac{\beta}{1+\beta}, \tag{5}$$

where $\beta \equiv \tau_p/\tau_s$. Fitting the data by Eq. (1)+Eq. (5) results, of course, in the same dependences as for d-wave pairing. The only difference is that the fitting parameter is now $\beta\lambda/(1+\beta)$, which correspondingly was found to be 0.046. If $\lambda=0.3$, then β is 0.18. For the $S=1/2$ impurities the latter value requires that the *exchange part of the impurity potential J be of the same strength as the potential part V*, independent of carrier concentration. This condition is not impossible, but quite unusual, because in conventional superconductors with magnetic impurities the J is from 3 to 10 times smaller than V.[7,21,27] The estimates of J in optimally doped YBCO give $J=0.13$ eV cell.[23] While this value is typical for conventional superconductors with magnetic impurities,[27] the criterion of applicability of the pair-breaking theory, $n_d J^2/E_F \ll T_{c0}$, is not satisfied. Moreover, J should further increase with decreasing x, since the observed δT_c increases, while the Fermi energy E_F decreases. Therefore, it seems unlikely that T_c suppression is governed by

spin-flip scattering because, at the required exchange interactions, the magnetic moments of in-plane O vacancies, if they exist, should strongly interact, leading to the formation of a spin-glass-like state above T_{c0} and reduction of the spin-flip scattering. Analysis of such situation, however, lies outside the scope of this paper.

The data on T_c suppression by Zn impurities (Fig. 5) seem to support the suggestion that in-plane O defects are nonmagnetic. For Zn impurities, the formation of localized magnetic moments (presumably on neighboring Cu atoms) was confirmed by a number of experiments (see Ref. 16 and references therein). However, in optimally doped YBCO, the induced moment was found to be fairly small ($\sim 0.2\mu_B$ per Zn) and thus can hardly be responsible for the strong T_c suppression. As seen in Fig. 5, the slope of T_c vs $1/\tau_{\rm imp}$ for Zn-doped YBCO with $x=0.93$ is only slightly higher than for in-plane oxygen defects. This small difference could possibly be due to a small additional contribution of magnetic pair breaking. The localized moment was found to increase up to $\sim 0.8\mu_B$ per Zn atom in $x=0.63$ samples,[16] which could explain why the slope of T_c vs $1/\tau_{\rm imp}$ for Zn-doped YBCO ($x=0.63$) is roughly a factor of 2 higher than that for in-plane oxygen defects. Note, however, that if the oxygen content in the Zn-doped crystals[16] is not perfectly constant, but could slightly decrease with z, then the observed T_c suppression by Zn would not be much different from what we observe for irradiated YBCO.

Another example of the system in which magnetic pair breaking is believed to play a major role in T_c suppression is $Y_{1-y}Pr_yBa_2Cu_3O_{6+x}$.[28] Strictly speaking, Pr impurities are not in-plane defects because they are located between the CuO_2 planes. However, it was found that Pr-localized $4f$ states hybridize with the CuO_2 valence band, leading to the filling, or localization, of holes in the planes. It was suggested that this hybridization generates the exchange interaction responsible for pair breaking. The effective magnetic moment was found to be $\sim 2.5\mu_B$ per Pr atom, consistent with a Pr^{4+} valence state.[28] It is clear however that Pr^{4+} substitution for Y^{3+} should also induce a strong potential scattering and thus pair breaking if the pairing symmetry is d wave. This scattering and pair breaking are presumably negligible for other rare-earth substitutions which are known to be in the R^{3+} state. Using the resistivity data on $Y_{1-y}Pr_yBa_2Cu_3O_{6+x}$ ceramics[28] and single crystals,[29] we plotted T_c as a function of the normalized residual resistivity, as shown in Fig. 5. The solid curve represents the best fit of our data on YBCO films with in-plane O defects by the pair-breaking theory [Eq. (1)+Eq. (4)]. Obviously, the data on Pr-doped YBCO fall on the same curve similarly to the data on Zn-doped YBCO. It is possible that, despite the different nature of the defects and despite the large difference in the impurity magnetic moments in these two systems, the scattering potentials combine in such a way as to provide the same value of β, but such a coincidence should be regarded as unlikely. Therefore, it is natural to suggest that in all the examples considered above T_c suppression is caused by impurity potential scattering because of d-wave pairing symmetry.

B. Phase fluctuations

While the pair-breaking mechanism can account for the defect-induced T_c suppression in HTS's, it is based on a Fermi-liquid description the applicability of which to cuprate metal oxides has not yet been proven. Recently, Emery and Kivelson[30] (EK) proposed a completely different explanation of T_c suppression which is not based on a picture of propagating quasiparticles and does not rely on any specific nature of defects, pairing mechanism, or symmetry. EK suggested that in superconductors with low superfluid density (''bad metals'') such as underdoped HTS's, T_c is controlled by the onset of a long-range phase order rather than by the mean-field pairing temperature. They showed that phase fluctuations reduce T_c of a ''bad metal'' with respect to the classical phase ordering temperature $T_\theta^{\max}$ according to

$$\ln(T_\theta^{\max}/T_c)=(\rho_{T_c}/\rho_Q)\ln(\varepsilon/T_c), \tag{6}$$

where ε is the energy scale of pairing interactions, ρ_{T_c} is the normal-state resistivity at $T=T_c$, and ρ_Q is some characteristic ''quantum'' resistivity which for HTS's was estimated as $\sim(3/8)hc/e^2\approx 1.1$ mΩ cm, where c is the c-direction lattice constant.

In order to compare the experimental data with the EK model, it is more convenient to rewrite Eq. (6) as

$$T_c=\varepsilon(T_\theta^{\max}/\varepsilon)^{1/(1-r)}, \tag{7}$$

where r is the ratio of the sheet resistance per CuO_2 plane, $R_\square$, at $T=T_c$ to the characteristic sheet resistance R_Q which separates superconducting ($R_\square<R_Q$) and nonsuperconducting ($R_\square\geqslant R_Q$) regime. The value of R_Q has recently attracted much interest. According to a number of data on various two-dimensional superconductors,[31–33] this critical resistance is close to, or somewhat higher than, the universal value $h/4e^2=6.45$ kΩ. Our data on irradiated YBCO ($x=0.9$) films suggest that T_c drops to zero at $\rho_0/\alpha\sim 300$ K. Since the typical α in the irradiated samples is in the range from 1.2 to 1.4 $\mu\Omega$ cm/K, the critical residual resistivity is ~ 400 $\mu\Omega$ cm, corresponding to $R_\square\approx 6.9$ kΩ. The same value was also found in Zn-doped YBCO ($x=0.63$) single crystals[16] and in irradiated Bi-2201 single crystal.[12] The critical residual resistivity in the underdoped YBCO thin films with in-plane O defects is higher (~ 1 mΩ cm at $x\approx 0.7$, and ~ 1.2 mΩ cm at $x\approx 0.6$), suggesting that the R_Q is somewhat material dependent. The difference in R_Q in different HTS samples can be due to the existence of macroscopic regions associated with structural defects or inhomogeneities which do not contribute to conduction and screening of charge fluctuations and thus lead to an apparent increase in R_Q, while the theory assumes a microscopically uniform ''bad metal.''

In Fig. 6 we presented T_c in YBCO with in-plane defects as a function of $R_\square$ extrapolated to $T=T_c$. To compare the data with Eq. (7), some of the parameters, or at least the variation range, have to be fixed. EK estimated $T_\theta^{\max}$ as 100–125 K for $x=0.9$ and suggested to set $\varepsilon\sim 1200$ K, which is the strength of exchange interaction in insulating parent compounds. It seems better to fix R_Q because this is the only parameter which can be measured. While the fits are quite insensitive to the variation of R_Q within $\sim 20\%$, for definiteness, we set $R_Q=6.9$ kΩ for the 90-K superconducting YBCO sample, a factor of 3 smaller value than that suggested by EK. As can be seen in Fig. 6, the data on Zn-doped single crystals can be perfectly fitted by Eq. (7). Fitting puts the ε in the range from 280 to 340 K and gives $T_\theta^{\max}=99$ and

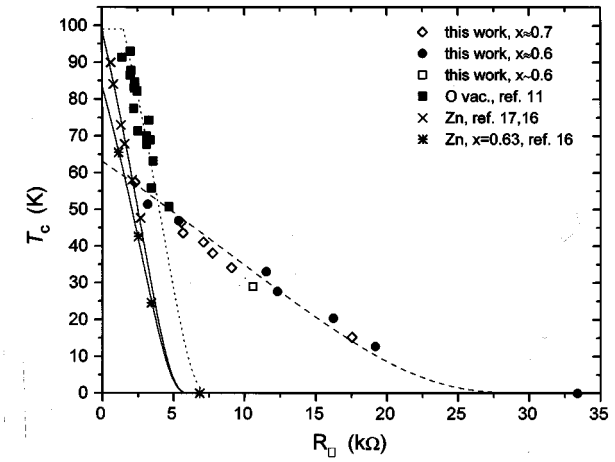

FIG. 6. Critical temperature of $YBa_2Cu_3O_{6+x}$ with different in-plane defects vs the sheet resistance per CuO_2 plane extrapolated to $T=T_c$. The different curves are the fits to phase fluctuation theory, as described in the text; solid and dotted curves correspond to $R_Q=6.9$ kΩ; the dashed curve corresponds to $R_Q=35$ kΩ.

83 K for the crystals with $x=0.93$ and 0.63, respectively. The data on irradiated fully oxygenated thin films[11] were obtained on different thin-film samples, and the data points therefore are more scattered.[34] The margins of fitting parameters are correspondingly broader. For instance, at $R_Q=6.9$ kΩ, the ε is 170 K and $T_\theta^{\max}=104$ K; for $R_Q=9.4$ kΩ, the ε is 280 K and $T_\theta^{\max}=110$ K. If ε is ~1200 K, then R_Q should be increased to ~19 kΩ. Note that a very good fit to the data on irradiated films can be achieved with the same set of parameters as for Zn-doped crystals (e.g., $R_Q=6.9$ kΩ, $\varepsilon=335$ K, $T_\theta^{\max}=99$ K) if we assume that the phase-fluctuation-induced T_c suppression starts working in these samples only when $R_\square$ exceeds some value $R_\square^*\sim 1.5$ kΩ. This fit is shown in Fig. 6. From the point of view of the phase diagram of HTS's suggested by EK, the existence of $R_\square^*$ would imply that those films are slightly overdoped and therefore are initially in the regime where T_c is determined by the mean-field pairing temperature T^{MF}, which presumably is weakly sensitive to disorder. Increasing disorder brings them down to the region where $T_\theta^{\max}<T^{\mathrm{MF}}$ and only then does T_c start to decrease. The T_c data on the irradiated underdoped thin films can also be well described by Eq. (7), though their $R_\square$ is higher than in Zn-doped single crystals with the same T_c, and thus fitting requires higher R_Q. As an example, in Fig. 6 we presented a curve corresponding to $R_Q=35$ kΩ, $T_\theta^{\max}\approx 63$ K, and $\varepsilon\approx 280$ K, which fits reasonably the data on both $x=0.7$ and 0.6 samples. The decrease in $T_\theta^{\max}$ agrees with the linear dependence of $T_\theta^{\max}$ on p, suggested by EK.[31]

It seems important to mention that the energy scale of pairing interactions suggested by the fits to EK theory is ~300 K, independent of the carrier concentration. This energy is remarkably close to the value of the pseudogap observed in optical measurements,[15] which was also found to be nearly composition independent, and to the value of the spin pseudogap (or T^*) suggested by susceptibility, NMR, and resistivity data. It is very likely, therefore, that different experiments point to the very same energy scale which is ultimately responsible for the superconducting pairing. Another conclusion which can be drawn from the data and fits presented in Fig. 6 is that there is no vivid qualitative difference between the T_c-vs-ρ_0 dependences following from the pair-breaking and the phase fluctuation mechanisms. Qualitatively different in only the asymptotic behavior at $T_c\to 0$, which is the most difficult region for a study because of the superconducting transition broadening and localization onset. We suggest, however, that the issue can be resolved by studying T_c suppression in the overdoped HTS's. Indeed, T_c suppression due to pair breaking should not be much different in overdoped HTS's from what was considered in Sec. III A, while a finite $R_\square^*$ increasing with overdoping should be observed if phase fluctuations are the prime mechanism.

IV. SUMMARY

We have studied the influence of oxygen defects (vacancies) in CuO_2 planes on the critical temperature T_c, resistivity, and Hall coefficient in $YBa_2Cu_3O_{6+x}$ thin films with T_{c0} ranging from 93 to 30 K ($x=0.9-0.5$). We have found that in-plane O defects have no influence on the features in resistivity and R_H which are associated with a spin-gap opening in underdoped cuprates. We have presented the analysis of T_c suppression in YBCO with in-plane O defects and in Zn- and Pr-doped YBCO as well as in electron-irradiated Bi-2201 and Bi-2212 high-T_c superconductors in terms of conventional pair-breaking theory. For all these HTS materials, we have shown that the observed T_c suppression is consistent with pair breaking by potential scatterers in d-wave superconductors, with the provision that the pair-breaking scattering rate be 3 times less than the transport impurity scattering rate following from the transport data. Anisotropic s-wave pairing can be ruled out. We have also presented some arguments and estimates which indicate that the defect-induced T_c suppression is unlikely to be due to localized magnetic moments, but only detailed studies of the magnetic properties of radiation defects in HTS's can completely resolve this issue. We have also demonstrated that the pair-breaking-based explanation of T_c suppression is by no means unique and that the data can equally well be described by the phase fluctuation theory proposed recently by Emery and Kivelson. These two mechanisms can possibly be distinguished by studying the defect-induced T_c suppression in overdoped HTS's.

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