Spectroscopic Signatures of Defect-Induced Pair Breaking in $Bi_2Sr_2CaCu_2O_{8+x}$

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We investigated the effect of disorder on the spectral properties of the high temperature superconductor $Bi_2Sr_2CaCu_2O_{8+x}$. We find that small defect densities, in the low 10^{-3} range, already suppress the characteristic spectral signature of the superconducting state, while new excitations appear within the gap. We conclude that, due to defect-induced pair breaking, superconducting pairs and normal carriers coexist below T_c. At higher levels of disorder the normal state is also strongly affected, and the quasiparticle features progressively smeared out. [S0031-9007(99)08924-3]

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Disorder affects the coherent state of a superconductor in characteristic ways. In conventional superconductors with isotropic pairing symmetry magnetic defects act as strong pair breakers [1], whereas nonmagnetic defects have negligible effect [2]. The scenario is radically different if the order parameter is anisotropic. For systems where the order parameter has line nodes in three dimensions (point nodes in two dimensions), even an infinitesimal amount of disorder leads to a finite density of states at the Fermi energy and hence to gapless superconductivity [3]. This result, initially obtained in the framework of p-wave superconductivity in the heavy fermions, was later extended to the high-T_c cuprates, following indications of anisotropic pairing in these materials. It is now theoretically established that pair breaking by nonmagnetic defects in the cuprates yields a residual density of states at the Fermi level and suppresses T_c [4–8]. There is a reasonable hope that studying the effects of disorder introduced in a controlled manner could provide important clues on the nature of the relevant interactions both in the normal and the superconducting (SC) states.

There is a growing consensus that, for hole-doped cuprates in the underdoped regime and up to optimal doping, carries pair with $d_{x^2-y^2}$ symmetry. The predicted sensitivity of $d_{x^2-y^2}$ pairing to nonmagnetic impurities, combined with the hypothesis of resonant defect scattering [9], naturally explain experimental results on disordered samples [4,10,11]. The hypothesis of resonant defect scattering in the cuprates is supported by recent theoretical results. t-J model calculations show that holes are bound to impurities in the strongly correlated CuO_2 planes, and that phase shifts approach $\pi/2$ for energies close to the bound state [12]. In the presence of strong antiferromagnetic fluctuations, nonmagnetic impurities may even have a stronger pair-breaking effect than magnetic ones [13]. Resonant scattering in the cuprates is also favored, for realistic values of defect potential strengths and concentrations, by the van Hove singularity (vHs) which occurs just below the chemical potential in $Bi_2Sr_2CaCu_2O_{8+x}$ [8].

Several experiments have probed the effects of disorder in the cuprates. Studies of Zn and Ni substitutional impurities in the CuO_2 plane showed that the nominally nonmagnetic Zn is more effective than magnetic Ni in suppressing superconductivity [14,15]. However, the pair-breaking mechanism is not definitely established by these results, because Zn may induce local magnetic moments when doped into the antiferromagnetic background [16,17].

Alternatively, defects can be introduced in a controlled way in the CuO_2 planes by irradiation. Irradiation with heavy ions or neutrons primarily creates columnar defects, and can be used to study flux dynamics and thermodynamic properties. Electron irradiation, on the contrary, introduces homogeneously distributed Frenkel-type point defects [18]. Although the nonmagnetic character of these defects is not yet fully established, there are strong indications that they suppress superconductivity due to potential scattering [19].

Changes induced by pair breaking in the electronic density of states near the chemical potential can be directly probed by high resolution angle-resolved photoemission (ARPES). In this Letter we report the first systematic ARPES investigation of $Bi_2Sr_2CaCu_2O_{8+x}$ with disorder introduced by electron irradiation [20]. By comparing samples which received different irradiation doses we could follow the evolution of the spectral function with disorder, both in the SC and normal phases. We find that new states appear within the SC gap in the disordered samples. The signal from these normal states increases with disorder, and is correlated with the suppression of the coherent SC spectral feature. At the lowest defect concentration, only the superconducting state is perturbed but, as disorder increases, the spectral properties of the normal states are also progressively affected.

Our samples were grown by the flux method [21]. Flakes of typical sizes of $5 \times 5 \times 0.3$ mm^3 were selected, and then heat treated in oxygen atmosphere at 600 °C , to obtain an identical optimal oxygen stoichiometry. All samples prior to electron irradiation had a T_c of 90 K. The electron irradiation was performed on a van de Graaf accelerator with an electron energy of 2.5 MeV. During irradiation, the samples were immersed in liquid H_2 and the irradiation flux limited to 3×10^{14} e/cm^2 in order to avoid sample heating above 21 K. Electron irradiation in these conditions displaces Cu and O atoms, resulting in an increase of resistivity and in a decrease of the critical temperature [18,19]. After warming up to room temperature, about 50% of the created defects are annealed leading to defect concentrations in the CuO_2 planes in the 10^{-3} dpa (displacements-per-atom) range. By varying the irradiation fluences we obtained critical temperatures of 82, 72, and 62 K.

ARPES experiments were performed in Lausanne by a Scienta 300 electrostatic hemispherical analyzer with an energy resolution of 10 meV and an angular acceptance of 1°. For photons of 21.2 eV this corresponds to $\Delta k \sim 0.04$ Å^{-1}. The samples were oriented by Laue x-ray diffraction, then transferred into the UHV system and cleaved *in situ* at a base pressure better than 2×10^{-10} torr. We performed measurements at 25 K in the SC state, and at 95 K in the normal state.

The resistivity curves of the pristine and irradiated samples as a function of temperature are shown in Fig. 1. The data were obtained on samples of $2 \times 0.5 \times 0.05$ mm^3, which were cleaved from the flakes used in ARPES, and mounted for four terminal resistivity measurements. The data are normalized to the room temperature resistivity value of the pristine sample. The resistivity increases with increasing irradiation dose and T_c is reduced. The T_c values (taken as the offset temperature of the resistivity) are the following: 90, 82, 72, and 62 K. The slope of the ρ-T curves for different doses is essentially the same, showing that the carrier density is the same for all samples and that just the static disorder increases with the irradiation dose, as indicated by the increase of the residual resistivity. The result supports the conclusions of previous Hall effect measurements [22].

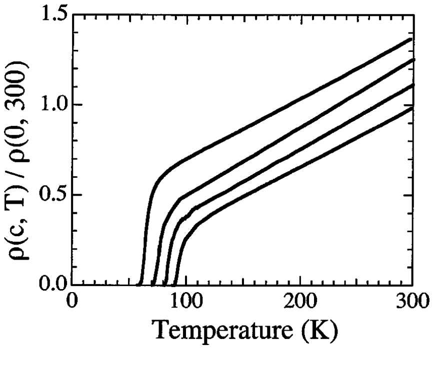

FIG. 1. In-plane resistivity vs temperature curves for the pristine (90 K) and irradiated (82, 72, and 62 K) samples, normalized to the resistivity of the pristine sample at 300 K.

Figure 2 illustrates the SC state spectra for three differently irradiated samples and a pristine sample (each specimen is identified by its T_c value). All data were collected close to the M $(\pi, 0)$ point [23] in the Brillouin zone, where the $d_{x^2-y^2}$ gap is maximum. The spectral signature of the SC state in ARPES is a coherent peak at a binding energy $E_B \sim \Delta$ (2Δ is the SC gap) followed by a dip and a hump at larger binding energies [24,25]. All spectra in Fig. 2(a) exhibit these characteristic features. The binding energy of the coherent peak is the same for all samples, irrespective of T_c, whereas its intensity decreases as T_c decreases, i.e., as the amount of disorder increases. In the irradiated samples, the leading edge is no longer resolution limited as in the pristine sample, suggesting the presence of new states in the gap. The high energy resolution of our spectrometer enables us to probe these low-energy excitations.

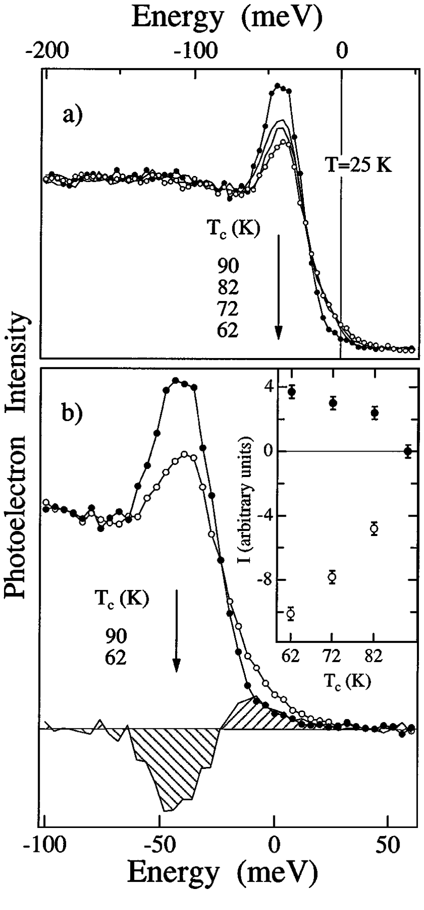

FIG. 2. (a) Superconducting state spectra (measured at 25 K) for the pristine (90 K) and irradiated (82, 72, and 62 K) samples, normalized at $E = -200$ meV; the 90 and 62 K spectra are also shown in (b) (notice the different energy scale) together with their difference. The inset shows the integrated areas of the positive and negative features of the difference curves vs T_c. The error bars reflect the uncertainty on the Fermi level position.

For a more detailed analysis of the defect-induced spectral changes it is useful to consider the difference curves between the spectra of the irradiated and the pristine samples. Figure 2(b) illustrates this analysis for the 62 K sample. The difference curve exhibits a prominent negative peak centered at ~ -40 meV, a positive feature near the Fermi level, and a null signal beyond -70 meV. These features are common to all the difference spectra. The absence of symmetric positive tails around the main negative peak rules out the possibility that the observed spectral changes are due to a mere broadening of the SC peak. Instead, the shape of the difference curves indicates the progressive appearance of excitations in the gap, and the concomitant reduction of the coherent peak intensity. To quantify these changes, we calculated the integrated intensities of the positive and negative features. The result of this analysis is shown in the inset, as a function of T_c. The signal from the gap excitations appears to grow with disorder. The loss of intensity from the SC peak is not entirely compensated by these new states, possibly because of scattering to higher binding energies and/or different wave vectors. Yet, the two processes are clearly correlated.

Both the loss of intensity in the coherent peak and the appearance of new states at the Fermi level are direct consequences of defect-induced pair breaking. The spectral feature near E_F indicates a small density of normal quasiparticle (QP) states obeying a Fermi-Dirac distribution. These QPs coexist with the SC condensate below T_c. There is a remarkable agreement between our results and the theoretical predictions by Fehrenbacher [7], who analyzed the effects of nonmagnetic defects on the SC state spectral function in a d-wave superconductor. Reference [7] argues that at the low defect concentrations considered here, resonant defect scattering dominates in a d-wave superconductor. In line with this hypothesis, we did not find any evidence for the opening of a gap in the d-wave nodal regions (data not shown), whereas gaps at these locations would be expected for nonmagnetic defect scattering in a highly anisotropic s-wave superconductor [6]. The observation that the energy of the coherent peak is the same for all spectra is also consistent with the small defect concentrations ($\sim 10^{-3}$ dpa). Shifts of the coherent SC peak to lower binding energies are indeed expected for higher disorder levels [6,20].

Figure 3 illustrates the normal state dispersion along the Γ-X $(\pi, -\pi)$ high symmetry direction (45° off the Cu-O bond directions). The pristine 90 K sample exhibits all features found in previous ARPES studies [24,25], namely, a fast dispersing state crossing the chemical potential at $\sim$35% of the Γ-X distance. The spectral line shape and dispersion are essentially identical for the 82 K sample—in contrast with the significant difference in the SC state (Fig. 1). On going from the 82 K to 72 K and to 62 K samples the normal state spectra progressively change. There is a loss of coherent intensity and a considerable broadening of the spectral features. Interestingly we observed similar spectral changes in neutron-irradiated samples of $Bi_2Sr_2CaCu_2O_{8+x}$ [26].

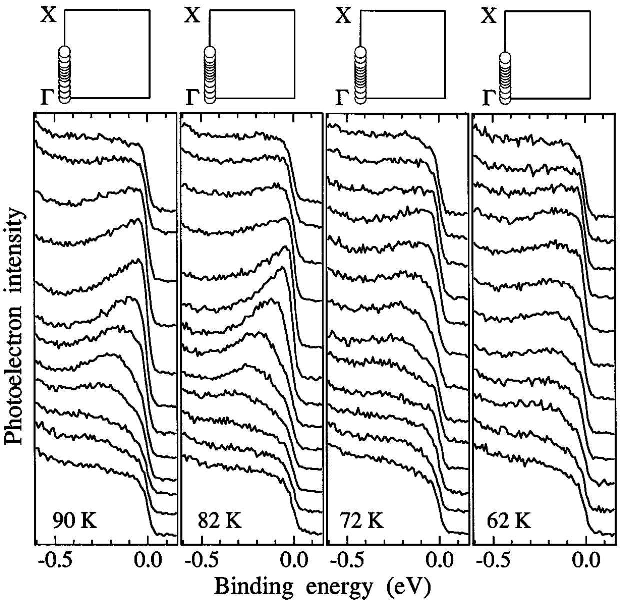

FIG. 3. Normal state spectra along the Γ-X $(\pi, -\pi)$ direction for the pristine sample and the irradiated samples. The insets indicate the locations in the Brillouin zone where the spectra were taken.

Along Γ-M-Z (data not shown) no Fermi surface crossing occurs. The QP states remain just below the chemical potential, forming the extended vHs, which we also observe in the irradiated samples. As noted above, the persistence of the vHs, which generates enhanced scattering rates, is relevant to the resonant scattering scenario [8].

We can only speculate on the nature of the changes in the normal state spectra. Qualitatively, it is tempting to associate the broadening of the QP peaks with a reduced lifetime, and a tendency to localization. However, to the best of our knowledge, the spectral signatures of weak localization have never been quantitatively investigated even in materials which can be described as normal Fermi liquids. Certainly they are not known in complex materials like the cuprates. The resistivity data of Fig. 1 indicate an increasing scattering in the irradiated materials, but do not show any sign of localization in the limited temperature range which can be explored before superconductivity sets in. Whatever the origin of the QP smearing, it is remarkable that a coherent excitation, albeit reduced, eventually develops in the SC phase. This observation calls for a theoretical explanation.

Finally, we notice that there are some similarities between the present results and the spectral properties of strongly underdoped $Bi_2Sr_2CaCu_2O_{8+x}$ [27]. In both cases a coherent SC spectral feature emerges from a normal state where QP peaks are unusually broad. Underdoping in $Bi_2Sr_2CaCu_2O_{8+x}$ is achieved by chemical substitution or oxygen reduction, and both procedures are likely to introduce disorder in the CuO_2 planes. Our data suggest that disorder could also play some role in these systems.

In summary, our ARPES data provide evidence for defect-induced pair breaking in a d-wave superconductor. The coexistence of superconducting and normal carriers is demonstrated by the observation of a residual density of states in the SC gap. Whereas the superconducting state is immediately affected, a clear influence of disorder on the normal state is visible only at higher concentrations. The present results indicate two directions for future research. On one hand, ARPES experiments probing in a quantitative way the effect of disorder in paradigmatic Fermi liquids systems, like some 2D transition metal dichalcogenides. On the other hand, a systematic comparison of the electronic properties of underdoped and irradiated cuprates with identical T_c values, with the goal of assessing the relative importance of disorder and reduced carrier concentration.

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