Electron tunneling and transport in the high-T_c superconductor $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$

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(Received 7 March 1994)

We have performed tunneling measurements on single crystals of the superconducting cuprate $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. With increasing concentration of Pr, the structure seen in $YBa_2Cu_3O_{7-\delta}$ in the energy region where a gap is expected, becomes even less pronounced (more "gapless") as the T_c is reduced. In the vicinity of the supeconductor-insulator transition, in tunnel junctions of demonstrably high quality, this structure becomes very weak. We draw upon a strong analogy between this system and ion beam damaged $YBa_2Cu_3O_{7-\delta}$ to discuss the results.

Tunneling measurements into the high-T_c cuprate superconductors have demonstrated a wide variety of results. Attempts to determine whether a conventional BCS energy gap exists have yielded both affirmative and negative answers and apparently depend upon the direction of tunneling, the nature of the tunnel junction, and the quality of the surface.[1] In contrast, the bismuthates $Ba_{1-x}K_xBiO_3$, $BaPb_{1-x}Bi_xO_3$, etc., apparently exhibit a well-behaved BCS energy gap with a ratio $2\Delta/kT_c$ close to the weak-coupling limit ($2\Delta/kT_c = 3.5 \rightarrow 3.8$).[2] Among the several differences between these two classes of compounds, dimensionality, proximity of antiferromagnetism, and coherence lengths stand out. In this work, we study a system in which two of these parameters can be systematically controlled in such a way that we can study their effect on the tunneling spectra. We find, in the system $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ that as we increase the praseodymium concentration, and consequently reduce the superconducting transition temperature T_c,[3] the tunneling spectra show an increase in gaplessness,[4] which can be interpreted either as a result of increased spin-flip scattering in a conventional s-wave superconductor[5] or elastic scattering for a d-wave order superconductor.

The system we have chosen to study is $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. In this system, which has been extensively studied, the Pr substitutes onto the Y site and T_c decreases monotonically until, at about $x = 0.55$ the material undergoes a superconductor-insulator transition.[3] The transitions remain sharp and the coherence lengths (both in-plane ξ_{ab} and out-of-plane ξ_c) increase by over a factor of 3.[6] With increasing coherence length in a conventional superconductor, it is expected that proximity effects (either intrinsic due to the planes or extrinsic due to the surfaces) should be less effective. Furthermore, with increasing Pr concentration it is found that there is increased carrier scattering. For substantial amounts of Pr, the resistivity data can be simply interpreted as an increase in the zero-temperature residual resistivity with almost no change in the temperature-dependent linear component α, i.e., $\rho \approx \rho_0 + \alpha T$.[7]

Since ρ_0 scales with Pr concentration, it is reasonable to treat this as an increased scattering rate and hence increased disorder. Therefore, in this system, the addition of Pr increases both the coherence length and the scattering rate in a controlled fashion as T_c reduces to zero.

The samples studied were single crystals. The $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ single crystals were grown using the following prescription.[8] First, precursors of the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ of nominal x value were prepared from high-purity (99.99% or better) Y_2O_3, Pr_6O_{11}, $BaCO_3$, and CuO powders. The stoichiometric mixtures were fired at 900 °C for 4 days, with intermediate grindings performed every 24 h. The precursors were then mixed with an excess of $BaCO_3$ and CuO to give a ratio of $(Y_{1-x}Pr_x)$:Ba:Cu of 1:9:24. The powder was loosely packed and placed in the high end of a ZrO_2 tray which was tilted at an angle of $\sim 15°$. The powder was heated at a rate of 100 °C/h to 880 °C, and then heated at a rate of 25 °C/h to 980 °C, where the temperature was held constant for 1 h. Next, the temperature was lowered at 6.2 °C/h to 880 °C and then cooled to 100 °C/h to room temperature. The crystals were mechanically extracted from the flux and annealed in flowing oxygen at 420 °C for 10 days. From electron microprobe analysis, the actual concentration of Pr was about 0.7 times the nominal concentration of the initial flux. Therefore, the concentrations of the crystals were determined by comparing their T_c's with high-quality polycrystalline samples whose Pr concentration was accurately known.[7]

Tunnel junctions have been prepared using two different techniques on surfaces normal to the c axis. We found that junctions meeting the criteria discussed below could be prepared either by a previously reported chemical etch[9] consisting of Br_2 in methanol or by low voltage-low angle ion milling followed immediately by evaporation of a counter electrode. For purposes of evaluation of the tunnel junction, we chose Pb as the counter electrode. Most of the junctions reported here were prepared using the chemical etch technique. A stringent measurement of the quality of the tunnel junction is the clear observation, not only of the superconducting energy gap of the counter electrode Pb and very low leakage current (less than 1 part in 10^4 for all junctions measured) below the Pb gap, but also at higher voltages of the structure associated with the electron-phonon coupling in Pb.[10] These

observations clearly confirm not only that the conduction process is tunneling, but that the tunneling is also a single step process such that the voltage across the junction is a measure of the energy of the injected electron or hole at least to voltages up to ≈ 10 mV. The junction area is typically ≈ 0.1 mm^2, and the junction resistances vary from 10 Ω to 10 KΩ. While there was a substantial difference in junction resistance as a result of different barrier preparation, it was found that the dI/dV vs V curves were identical after scaling the resistance. This result gives further confidence in the conclusion that the tunneling was an elastic process and that these measurements are not a result of surface effects.

In Fig. 1 we show the results of measurements on three separate (nominal) concentrations; $x=0$, 0.28 and 0.46 corresponding to $T_c=92$, 63, and 37 K. Plotted in Fig. 1 are the tunneling conductances for these three concentrations separately normalized at a voltage of -150 mV. In order to eliminate the structure from the Pb, we either did the measurement at 1.5 K with a small magnetic field of 0.1 T applied to drive the counter electrode Pb into the normal state, or raised the temperature to about 10 K (just above the T_c of Pb which is 7.2 K). Aside from the additional thermal smearing associated with the higher-temperature method, the two procedures were equivalent. These data are reproducible on junctions which meet the criteria of quality discussed above (both superconducting energy gap of Pb and characteristic signature of electron-phonon coupling in Pb observed). We have measured at least three samples for each of the above Pr concentrations, and despite the variation in junction resistance, we observe the same tunneling conductance curve for each concentration upon normalizations (at -150 mV for example). The concentration variation illustrated in Fig. 1 is faithfully reproduced as the data is representative of a more extensive set of curves of varying Pr concentrations over the entire range from $T_c=92$ K to the superconductor-insulator transition. The undoped ($x=0$) curve is similar to that observed previously[9] and by other investigators.[11] The linear background conductance is apparent[4] as is the structure in the voltage region where an energy gap would be expected for a BCS superconductor. The BCS ratio $\Delta/kT_c=1.76$ implies an energy gap of 13.9 meV, the range over which structure is observed, but the data show no gap. In addition to the peak in the conductance at ≈ 18 mV, there is also an additional structure at lower voltages of ≈ 4 mV. We will come back to this later.

For the samples with increasing Pr concentration, we see that this structure in the vicinity of an expected BCS energy gap becomes less pronounced. If proximity effects were dominating the observed structure (due either to extrinsic surface efforts or intrinsic spatial variation of the order parameter inside the crystal structure) we would expect these proximity effects to be less effective with increasing x because of the increasing coherence length. This would result in a more conventional structure for lower T_c. This is not what is observed as the material is apparently more "gapless" with increasing Pr substitution.

To more clearly illustrate this, we have normalized the linear background of the data in Fig. 1 and present the results in Fig. 2. The curves in Fig. 2 were acquired by dividing the data in Fig. 1 by a linear background conductance. This is determined by extrapolating to zero bias from high voltages (75–150 mV). We note that using this procedure we recover a conductance where it appear that "states are not conserved." We are not too

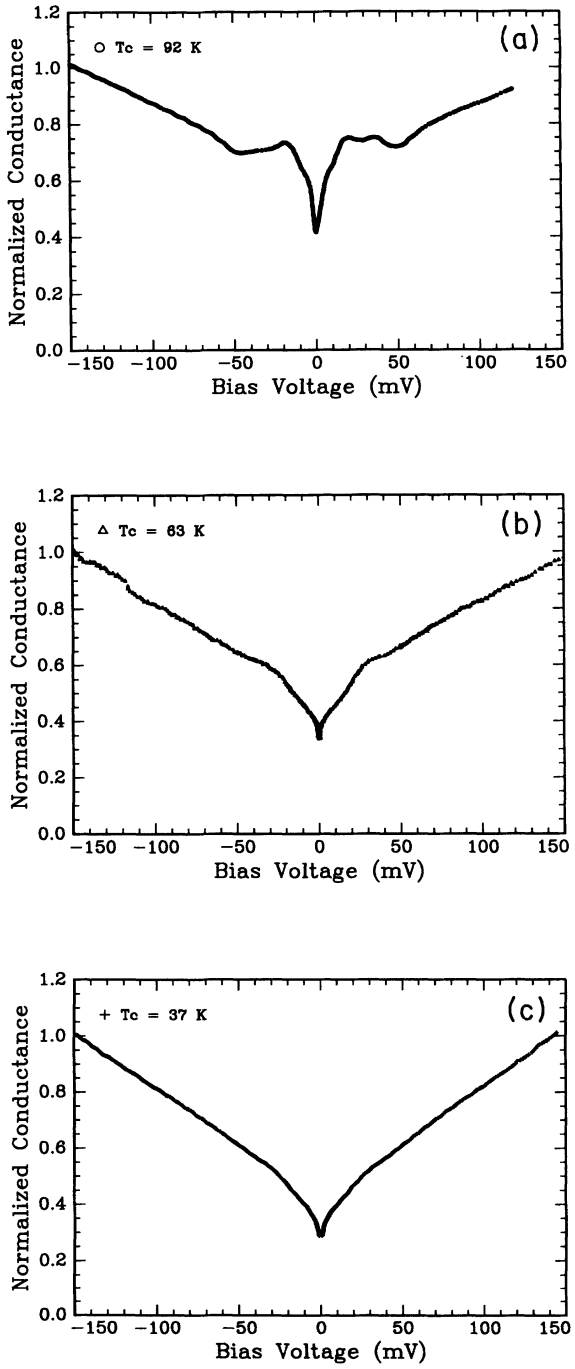

FIG. 1. Normalized tunneling conductance (normalized at -150 mV bias) for three selected compounds of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. The x values for the three curves are (a) $x=0$, (b) $x=0.28$, (c) $x=0.46$.

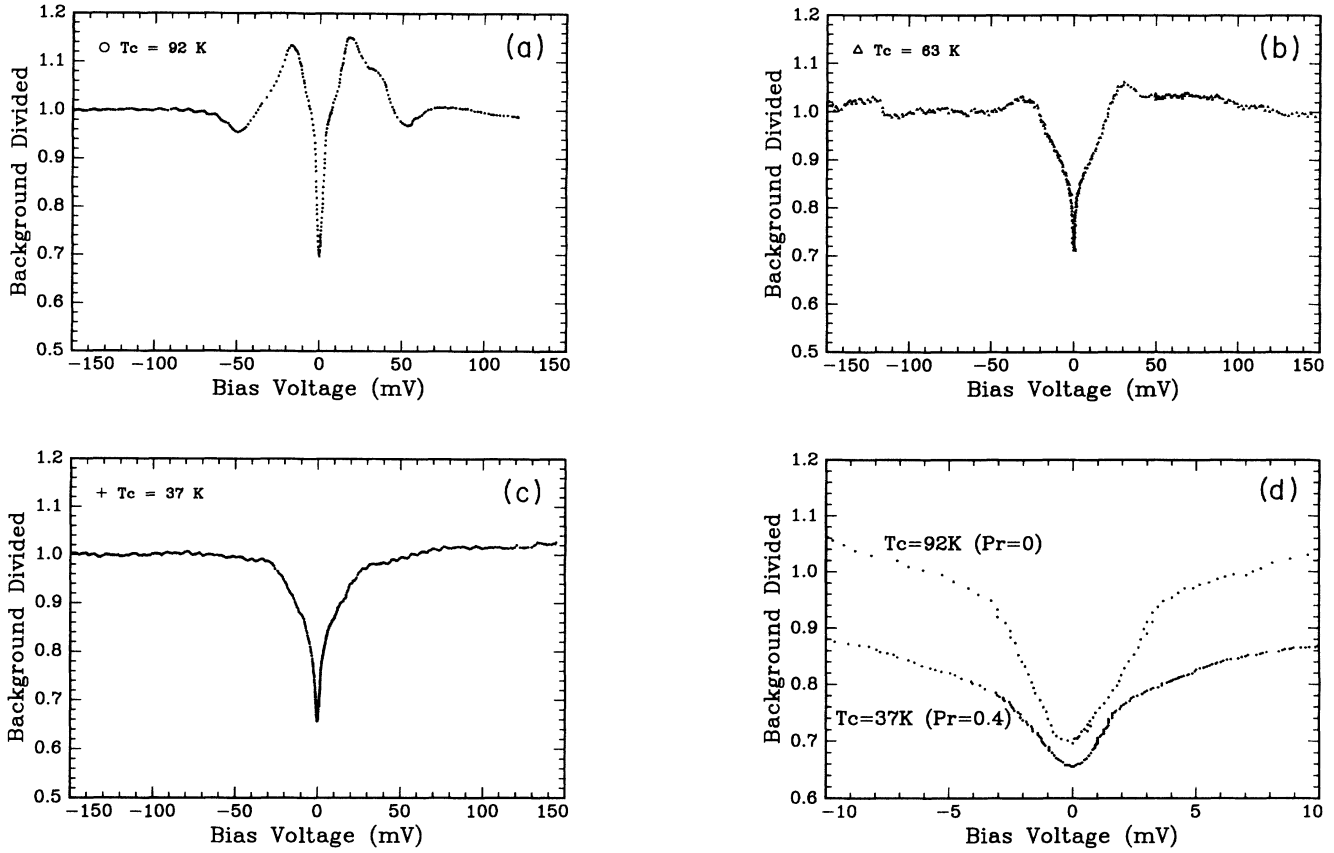

FIG. 2. The same data of Fig. 1 with the linear background at high voltages removed. (a) $x=0$, $T_c=92$ K, (b) $x=0.28$, $T_c=63$ K, (c) $x=0.46$, $T_c=37$ K, (d) Expanded voltage scale for frames (a) and (c).

worried about this apparent problem because satisfying this "sum rule" depends upon the choice of normalizing linear background. If the missing states are distributed over a wide energy range (up to say 100 mV or so), we could normalize them out. We have tested this using different voltage regions to normalize the linear background and find this to be the case. The structure in the $YBa_2Cu_3O_{7-\delta}$ apparent at 18 mV becomes less pronounced with increasing x. We caution against the simple conclusion that this structure is simply broadened by lifetime effects, however. In addition to the peak in the conductance at ≈ 18 mV, there is also a characteristic which could be interpreted as a "second gap" at lower voltages (≤ 5 mV). This structure for $x=0$ and $x=0.46$ is shown more clearly in Fig. 2(d) where we reiterate the point made above. If, with increasing x, the structure was simply broadened, we would expect the low-energy characteristics to disappear first which is apparently not the case. We have previously speculated[9] that this structure was associated with a highly anisotropic gap in the c direction (as opposed to the a-b plane), and while these data are not strong evidence for or against that speculation, it is interesting that it is apparently more robust than the higher-energy structure at 18 mV. We reiterate that none of this represents a true "gap" as the tunneling density of states remains finite at zero bias. Nevertheless, this low-energy structure is apparently less sensitive to the substitution of Pr than the higher voltage structure which almost disappears for $x=0.46$.

There has been substantial discussion recently over the possibility of d-wave superconductivity in these cuprates as opposed to a highly anisotropic, more conventional pairing mechanism.[12] It is indeed tempting to interpret the data of Figs. 1 and 2 in terms of d-wave pairing and the impact of elastic scattering on that pairing. To pursue this issue further, we show in Fig. 3(a) a family of $\rho(T)$ curves for the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system.[3] It is striking that, with increasing Pr doping, $\rho(T)$ retains its linear dependence but with an increasing residual resistivity ρ_0 characteristic of a conventional metal with impurity scattering. Within the framework of d-wave superconductivity, impurity scattering results in gaplessness due to rapid scattering from positive to negative values of the energy gap, resulting in an "average." For rapid enough scattering, the average becomes zero for d-wave symmetry and superconductivity disappears.

We show a remarkably analogous set of curves in Fig. 3(b) which were generated from ion-beam damage in $YBa_2Cu_3O_{7-\delta}$.[13] Here also, $\rho(T)$ retains its linear behavior with an increased residual resistivity. The quantitative similarity of these two data sets is striking. While the width of the superconducting transition is larger in

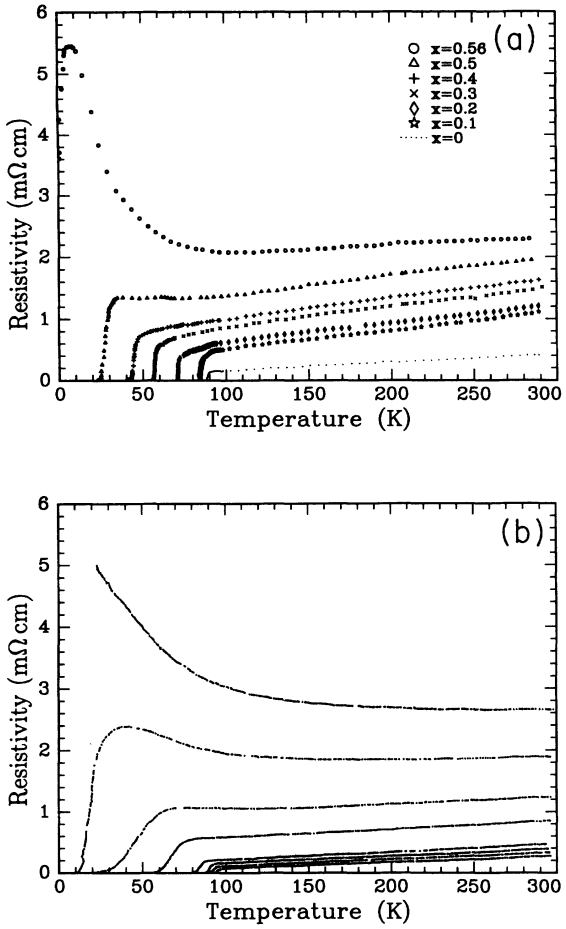

FIG. 3. Resistivity vs T for (a) $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$: For increasing Pr the T_c drops and the residual resistivity increases, (b) Ion damaged $YBa_2Cu_3O_{7-\delta}$. After bombardment of 1-MeV Ne^+ ions at fluences of (0, 0.1, 2.5, 4.0, 10.0, 15.0, 20.0, and 22.0)$\times 10^{13}$ ions/cm^2. For increasing ion damage the behavior is similar for increasing Pr in (a).

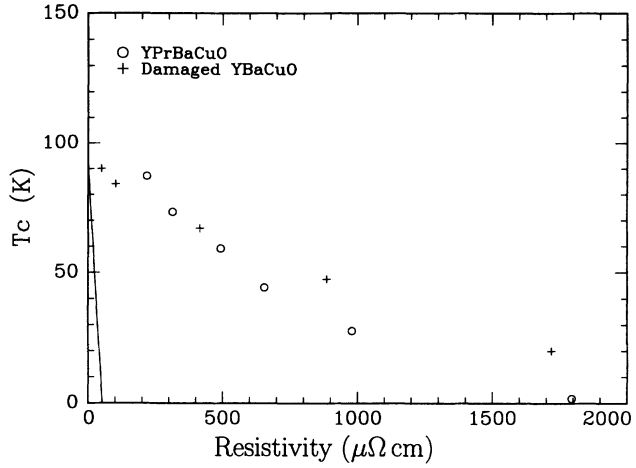

FIG. 4. T_c vs residual resistivity from the data of both Figs. 3(a) and 3(b). The solid line is our estimate of T_c vs resistivity for d-wave pairing.

the ion damage case the general features are strikingly similar. The T_c decreases in a similar fashion and the superconductor-insulator transition occurs at the same residual resistivity. More quantitatively, we can look at the variation of T_c with residual resistivity and that is shown in Fig. 4. The analogy between Pr substitution and ion damage is even more compelling as we see that T_c apparently is dependent on ρ_0 in both cases and not particularly sensitive to the method ρ_0 is generated. Using a very simple model, we can estimate a scattering rate from the determination of ρ_0. While this can only be considered qualitative, it is useful to determine relative scattering rates. In a recent calculation, Jiang, Carbotte, and Dynes have used a generalized Eliashberg formalism valid for a d-wave superconductor and determined the quasiparticle density of states including scattering.[14] Indeed the magnitude of the "gap" structure was sensitive to elastic scattering but our simple estimate of $1/\tau_{\text{impurity}}$ determined from the values of ρ_0 in Fig. 3 suggests a scattering rate an order of magnitude or two larger than that needed to suppress d-wave pairing. The solid line intersecting $T_c=0$ at 50 $\mu\Omega$ cm is our estimate of where T_c should go to zero if d-wave pairing is responsible. This analogy implies that superconductivity is destroyed for a scattering rate $E_F\tau\approx\hbar$ and *not* $\Delta\cdot\tau\approx\hbar$ as expected for d-wave pairing. Another way to think about this is that since the T_c is so *insensitive* to scattering, any coupling mechanism that is sensitive to structure in k space is probably not relevant. The k-space structure has disappeared at much lower scattering rates. Such a k-space dependence is implied in the model of spin-wave fluctuation-induced superconductivity. Alternatively, if we interpret the data of Fig. 1 as due to gaplessness as a result of spin-flip scattering, again a small fraction of the scattering as determined from the residual resistivity ρ_0 can be spin-flip scattering. It is, indeed, tempting to interpret this collapse of the structure as due to one of the two processes; either elastic scattering in a d-wave superconductor or spin-flip scattering in an anisotropic s-wave superconductor. As discussed above, there are quantitative problems with both these interpretations.

It is important, finally though, to remember that through this strong scattering and disappearance of structure in the region where a "gap" is expected, a low-energy signature at 3–5 mV persists.

The superconductor-insulator transition of Fig. 3 is reminiscent of that extensively studied in two-dimensional quench condensed conventional superconductors.[15] With increasing disorder, T_c is reduced until the sheet resistance is of the order of 10 000 $\Omega/\square$ at which time $T_c\rightarrow 0$ and the superconductor-insulator transition results. The analogy with the data of Fig. 3 is even more striking if we assume that the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ is really comprised of two-dimensional (CuO_2) sheets. With increasing disorder (Pr substitution or ion damage) the resistance/$\square$ increases, T_c decreases and the superconductor-insulator transition results. Indeed, the superconductor-insulator transition occurs at $R_\square\approx 10$ KΩ per CuO_2 sheet; a *quantitative* similarity with conventional two-dimensional (2D) superconductors. From this perspective, it is not surprising an

insulating transition occurs and superconductivity disappears in the cuprates; we do not know of a 2D conventional superconductor with an $R_{\square}$ greater than 10 K Ω. There are, however, additional considerations as the conventional 2D superconductors are known to retain their BCS gap until very close to the superconductor-insulator transition.[16]

In summary, we have studied the properties of the system $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ using electron tunneling. Although with increasing x, the coherence lengths ξ_{ab} and ξ_c both increase, the tunneling structure in the energy range where a gap might be expected decreases in strength rather than increases. This could be interpreted either as elastic scattering for a d-wave superconductor or spin-flip scattering in an anisotropic conventional superconductor. The transport properties of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ are remarkably analogous to those of ion damaged $YBa_2Cu_3O_{7-\delta}$ and a very simple relationship between the residual resistivity ρ_0 and the T_c results. Furthermore, if we think of these cuprates as two-dimensional conductors, the quantitative similarity of these results with the studies of superconductivity in conventional materials when reduced to two dimensions is even more striking.

We thank F. Sharifi and R. P. Barber for advice and assistance, and I. K. Schuller, F. Hellman, J. Valles, and Steve Kivelson for valuable discussions. This work is supported by the Air Force Office of Scientific Research (AFOSR) Grant No. F4962 092 J0070), the NSF (Grant No. DMR 91-13631), and the U.S. Department of Energy (Grant No. DE-FG03-86ER45230).

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