Large in-plane Elastic Scattering due to Cu-vacancies in an Electron Doped Superconductor

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Abstract. High transition temperature (high-Tc) superconductivity arises in cuprate materials when sufficient holes or electrons are doped into the CuO₂ layers of their antiferromagnetic (AF) insulating parent compounds. While hole doping immediately turns the material superconducting, mere electron doping is not enough to induce superconductivity in some of the cuprates which need to be annealed in a low oxygen environment in order to induce superconductivity. In this work we analyse STM spectra on an electron doped superconductor, Pr₁₋ₓLaₓCeₓCuO₄/g₁₄₇/g₃₀₃ (PLCCO), and show that compared to their hole doped counterparts, these electron-doped materials show a significant in-plane elastic scattering component. Since the copper deficiencies are intrinsic to PLCCO these could be the main source of the high in-plane scattering rate.

1. Introduction

An important test of the properties of the superconducting state is how non-magnetic and magnetic impurities affect it. There have been extensive theoretical [1,2,3] and experimental [4,5,6] studies of impurities in conventional superconductors. According to the pioneering work of Abrikosov and Gor’kov[1] and its extensions [2,3], although both magnetic and non-magnetic impurities are pair breakers in conventional superconductors, non-magnetic impurities have a weaker effect compared to magnetic impurities [4]. A magnetic perturbation in a conventional superconductor reduces the superconducting order parameter and leads to the appearance of quasiparticle excitations within the superconducting gap. Just the opposite is however expected to be true in the case of high-Tc cuprates, where magnetic impurities are predicted to have a weaker effect on superconducting properties [7,8]. In the high Tc cuprates however, these effects are difficult to discern from macroscopic measurements. For example, with the exception of Zn, resistivity and other bulk measurements indicate that both magnetic and non-magnetic impurities have similar effects on superconductivity [9,10,11,12]. Local probes like STM are therefore crucial to measure impurity effects on high Tc cuprates [4,7,13].Our approach in this paper is to obtain information on the quasiparticle scattering rate of PLCCO by analysing the lineshape of the STM spectra.
Superconductivity in electron doped materials arises within very narrow (10% to 18%) range of electron concentration. Our samples are optimally doped; 12% of trivalent Pr$^{3+}$ is replaced by tetravalent Ce$^{4+}$. However, unlike their hole-doped counter parts mere doping is not sufficient to induce superconductivity in electron doped cuprates. They need to be post annealed. PLCCO samples used in this study were post annealed to 970°C under an Ar environment to achieve the superconducting transition temperature $T_c = 24$ K. Samples were cleaved in ultra high vacuum and inserted into the STM head held at 4K. From our previous studies [14,15], although the PLCCO surface lacks atomic scale features, it is possible to get reproducible differential conductance ($dI/dV(r,eV)$) spectra from these samples. Figure 1 shows typical spectra obtained at different locations on PLCCO. Inhomogeneity, which is one of the hallmarks of high-$T_c$ cuprates, is clearly visible in the figure as the spectra have different superconducting gaps. Our first observation is that compared to the prototypical hole-doped cuprate Bi$_2$Sr$_2$CaCu$_2$O$_{8+}$ (Bi2212), the coherence peaks in this electron-doped sample are highly suppressed. Qualitatively, this indicates an increased scattering rate in PLCCO compared the Bi2212. However, in order to establish the magnitude and possible origins of this scattering we seek to obtain more quantitative information. Since there is no established microscopic theory for cuprate superconductors, we use a simple phenomenological picture to capture the spectral line shape [16,17]. This model captures the momentum space (k-space) variation in the superconducting gap [18,19] due to its d-wave symmetry.

Figure 1: Typical STM spectrum taken with atomically resolved STM. Each spectrum is an average of five neighbouring spectra.

Modifying the BCS equations to account for d-wave pairing symmetry is straightforward and was done by K. Maki [20]. The tunnelling conductance is equivalent to the local density of states and can be written in terms of extended BCS theory for d-wave pairing as:

$$\frac{dI}{dV}(E, T) = \int_0^\pi d\theta \text{Re} \left( \frac{|E-i\Gamma|}{\sqrt{(E-i\Gamma)^2-(\Delta/T)^2+\cos^2(2\theta)}} \right)$$

Where, "$f$" is Fermi Dirac distribution function at temperature $T$, $E=eV$ is the quasiparticle energy, $\Gamma$ is quasiparticle scattering rate, and $\Delta$ is superconducting gap.
2. Energy Independent Scattering Rate

First we assume that the scattering rate has no energy dependence. By best fitting the integrated density of states for d-wave symmetry with the tunneling spectra we obtain the superconducting gap, \( \Delta \) and the quasiparticle scattering rate, \( \Gamma \). Figure 2(a) shows the typical fit between theory and data. The histogram of \( \Gamma \) extracted from more than a thousand tunnelling spectra is shown in Figure 2(b). It is found that the mean value of the \( \Gamma \) is 2.8±0.76 meV. However, we find that the fits to our data with \( \Gamma \) held constant are not perfect. We therefore turn to similar studies on hole-doped cuprates. In Bi\(_2\)Sr\(_2\)Ca\(_2\)Cu\(_2\)O\(_8\) (BSCCO2212), Alldredge et. al. reported that for an extensive doping range (8% to 22%) the constant scattering rate from near unitary scatterers plays only a subsidiary role. In contrast they find that using an energy dependent effective scattering rate (\( \Gamma = \alpha \Delta \)), plays a key role at low temperatures [17]. Surprisingly, in our case we were not able to fit our spectra with the simple effective scattering rate, \( \Gamma = \alpha \Delta \). Instead, as shown in Figure 3 (a), the best fits were obtained with the combined scattering rate scattering rate \( \Gamma = \Gamma_1 + \alpha \Delta \).

This combined scattering rate is similar to that seen in angle resolved photoemission spectroscopy studies of underdoped Bi2212 used by Kaminski et al [21]. Similar to our observations, their studies indicate that the functional form of the scattering rate for underdoped and optimally doped samples has both energy independent and energy dependent parts with the constant \( \Gamma_1 \) arising from the elastic contribution to scattering and the coefficient \( \alpha \) representing the inelastic contribution. The histogram of inelastic scattering coefficient \( \alpha \) is shown in Figure 3(b). The inelastic processes arise from exchange of dynamic spin fluctuations or phonons, whereas the elastic scattering can arise from impurities and disorder within the copper oxide planes (in-plane impurities) or from impurities in the neighbouring metal oxide planes (out-of-plane impurities). Scattering by out-of-plane impurities for example, has been claimed to be responsible for the electronic nanoscale inhomogeneity in the superconducting gap [22,23] We find that unlike the hole doped cuprates, the in-plane constant elastic scattering (\( \Gamma_1 \)) is much higher in PLCCO. \( \Gamma_1 \) has an average value of 1.5 meV, which is approximately 20% of the mean superconducting gap.

![Figure 2.0: (a) Best fit with PLCCO spectra at 5 K using constant scattering rate \( \Gamma \) and (b) the histogram of \( \Gamma \) obtained from 1024 STM spectra](Image)
3. Sources of constant elastic scattering:
The high-temperature synthesis process of electron doped superconductors creates a Cu deficiency (~1%) in some of the as-grown electron doped cuprates[24, 25]. Kang et. al. suggested that these vacancies behave like the Zn impurities and locally destroy superconductivity [26]. While the post-annealing process repairs some of these vacancies, we expect that not all vacancies are repaired in the 24K PLCCO samples resulting in strong elastic scattering which is responsible for the large value of $\Gamma_1$.

![Figure 3.0: (a) Best fit with PLCCO spectra at 5K using $\Gamma = \Gamma_1 + \alpha E$. (b) $\alpha$ histogram obtained by fitting dI/dV spectra.](image)

4. Conclusion:
We have found a very high constant in-plane elastic scattering rate in the electron doped superconductor PLCCO. Since this is not detected in the hole-doped counterparts, the constant elastic scattering is intrinsic to electron doped superconductors. Cu vacancies, which are naturally present in electron doped superconductors, act like non-magnetic impurities and can have a strong detrimental effect on superconductivity. Our experimental data indicate that most of the scattering in PLCCO occurs in the CuO$_2$ planes by non-magnetic unitary scatterers, which can be potentially attributed to these Cu vacancies.

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