Oxygen Chain Disorder as the Weak Scattering Source in YBa$_2$Cu$_3$O$_{6.50}$

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The microwave conductivity of an ultra-pure single crystal of YBa$_2$Cu$_3$O$_{6.50}$ has been measured deep in the superconducting state as a continuous function of frequency from 0.5 → 20 GHz. Conductivity spectra were first measured at four temperatures below 10 K after having prepared the crystal in the so-called ortho-II phase in which the CuO chain oxygen are ordered into alternating full and empty chains. These spectra exhibit features expected for quasiparticle scattering from dilute weak impurities (small scattering phasenvelope) in an otherwise clean d-wave superconductor. The measurements were repeated on the same crystal after heating and then rapidly quenching the sample to reduce the degree of oxygen order in the CuO chains. With the increased disorder, the conductivity spectra retain the distinctive weak-limit scattering features, but have increased widths reflecting an increase in quasiparticle scattering. These measurements unambiguously establish that CuO chain oxygen disorder is the dominant source of in-plane quasiparticle scattering in high purity YBCO.

Disorder and inhomogeneity play crucial roles in determining the behaviour of many measurable properties of the cuprates. Early on, cation substitution in the CuO$_2$ planes was found to have striking effects on low temperature properties such as the magnetic penetration depth, and scanning tunneling spectroscopy (STS) has provided detailed tests of the influence of point-like defects on d-wave superconductors. More recently, attention has been focused upon the puzzling effects of off-plane disorder. Fujita et al. have shown that off-plane cation disorder has a substantial impact on the critical temperature $T_C$. STS measurements by McElroy et al. on Bi$_2$Sr$_2$CaCu$_2$O$_{8+y}$ (BSCCO) have provided evidence that interstitial dopant oxygen atoms are correlated with mesoscale variation in the electronic spectrum. In this context YBa$_2$Cu$_3$O$_{6+y}$ (YBCO) offers a unique opportunity to study the influence of defects, since high purity crystals of YBCO can be grown with negligible cation disorder both on- and off-plane. Like BSCCO, YBCO’s doping can be controlled via off-plane oxygen atoms, but in YBCO these dopants are organized into CuO$_y$ chains whose filling and degree of disorder can be systematically manipulated. For instance, YBa$_2$Cu$_3$O$_7$ has filled CuO chains that provide a slightly overdoped 85 K superconductor with very low disorder. At $y = 0.5$ one can prepare a stable phase with alternating filled and empty CuO chains (ortho-II superstructure) that also can have very little disorder. Above 100°C, the ortho-II phase gives way to the ortho-I phase in which all CuO chains are equally occupied. Because oxygenation of YBCO is negligibly slow below 300°C, a low-temperature anneal at 200°C followed by a rapid quench can change the level of disorder in the CuO chains without changing the total oxygen content. In this article, we demonstrate that oxygen disorder in the CuO chains is the dominant source of quasiparticle scattering at low temperature in YBa$_2$Cu$_3$O$_{6.50}$.

We have recently developed a non-resonant broadband microwave apparatus capable of measuring the surface resistance $R_s$ of ultra-low-loss samples continuously from 0.5 → 22 GHz. With a separate measurement of the penetration depth $\lambda(T)$ the real part of the electrical conductivity $\sigma_1(\omega, T)$ can be extracted from these data. We start with a detwinned YBa$_2$Cu$_3$O$_{6.50}$ crys-
To complete our data analysis, we use \( \lambda_a(T \to 0) = 202 \pm 22 \text{ nm} \) and \( \lambda_b(T \to 0) = 140 \pm 14 \text{ nm} \) for ordered YBa\(_2\)Cu\(_3\)O\(_{6.50}\) as obtained from recent zero-field ESR measurements on Gd-doped Gd\(_y\)Y\(_{1-x}\)Ba\(_2\)Cu\(_3\)O\(_{6+y}\)\(^{10}\). There are no reported measurements of \( \lambda(T \to 0) \) for YBCO with disordered chain oxygen atoms. A reasonable estimate of these values was obtained by requiring that the low-\( T \) slope of \( 1/\lambda^2(T) \) remain constant upon disordering the CuO chains, as suggested by recent \( H_{c1} \) measurements on underdoped YBCO\(^{11}\). This analysis yields \( \lambda_a(T \to 0) = 238 \pm 24 \text{ nm} \) and \( \lambda_b(T \to 0) = 162 \pm 16 \text{ nm} \) for disordered YBa\(_2\)Cu\(_3\)O\(_{6.50}\). These values of \( \lambda(T \to 0) \) are consistent with the relationship between \( T_c \) and \( \lambda(T \to 0) \) derived from the ESR measurements on YBCO\(^{12}\). We emphasize that \( \lambda(T \to 0) \) merely sets an overall scale factor for the \( \sigma_1(\omega, T) \) spectra and its value in no way alters the key conclusions of this work.

FIG. 2: (a) Top panel: Measured \( \hat{a} \)-axis surface resistance of YBa\(_2\)Cu\(_3\)O\(_{6.50}\) with highly ordered CuO chains. Bottom panel: Extracted \( \hat{a} \)-axis quasiparticle conductivity spectra. The solid lines are phenomenological fits to the data. The inset compares the oscillator strength obtained from the integrated conductivity to that obtained from \( \lambda \). (b) Top panel: Measured \( \hat{a} \)-axis \( R_s \) of YBa\(_2\)Cu\(_3\)O\(_{6.50}\) with disordered chain oxygen. Bottom panel: Extracted \( \hat{a} \)-axis quasiparticle conductivity spectra. The solid lines are phenomenological fits to the data. Inset: There is no change in the total integrated oscillator strengths before and after disordering the chain oxygen.
Figure 1 shows the measured change in the cavity resonant frequency $\Delta f_r(T) = f_r(1.5 \text{ K}) - f_r(T)$ due to the YBa$_2$Cu$_3$O$_{6.50}$ sample both before and after disordering the CuO chain oxygens. The hole doping of the CuO$_2$ planes in YBCO is not a unique function of the oxygen content $y$, but depends both on $y$ and the CuO chain ordering. The observed shift in $T_c$ from 55 to 49 K upon disordering the CuO chains is due solely to a change in the hole doping of the CuO$_2$ planes. For $T < T_c$ the measured $\Delta f_r(T)$ is proportional to the change in the penetration depth $\Delta \lambda(T)$. The inset of Fig. 1 shows that $\Delta \lambda_a(T) \propto T$ for both ordered and disordered CuO chains. The measured crystal is a platelet with dimensions $a \times b \times c = 0.482 \times 0.741 \times 0.028 \text{ mm}^3$. A small contribution from $\Delta \lambda_c(T)$ was removed by using previous measurements of $\Delta \lambda_c(T)$ for a YBa$_2$Cu$_3$O$_{6.60}$ ($T_c = 60 \text{ K}$) crystal together with the determination of the doping dependence of $\lambda_c(0)$ by Homes et al. The low-$T$ slope of the corrected $a$-axis data is $d(\Delta \lambda_a(T))/dT = 1.36 \pm 0.10 \text{ nm/K}$ which is comparable to a previously measured value of 1.05 nm/K found for a platelet with a larger $a:b$ aspect ratio that did not require $c$-axis corrections.

The top panel of Fig. 2a shows the measured ortho-II-ordered $a$-axis surface resistance. To a very good approximation the conductivity is proportional to $R_s/\omega^2$ and is given by $\sigma_1(\omega, T) \approx 2R_s(\omega, T)/\mu_0^2\omega^2\lambda^3(0)$. In practice, a more complete analysis that accounts for the temperature dependence of $\lambda(T)$ and self-consistently includes screening due to the quasiparticle conductivity is used.
to extract $\sigma_1$ from the $R_s$ measurements. The conductivity spectra obtained by the full analysis are shown in the bottom panel of Fig. 2. These spectra are fit to a phenomenological model $\sigma_1 = \sigma_0/[1 + (\tau \omega)^\beta]$ which captures the observed lineshapes very well and gives a measure of the spectral width $\tau^{-1}(T)$.

As previously observed for a different sample, the ordered YBa$_2$Cu$_3$O$_{6.50}$ conductivity data exhibit qualitative features expected for $d$-wave quasi-particles undergoing weak-limit scattering: cusp-like lineshapes, temperature independent $\sigma_1(\omega \to 0)$ intercepts, and $T$-linear spectral widths $\tau^{-1}(T)α$. The measured $\hat{a}$-axis $R_s(\omega, T)$ and $\sigma_1(\omega, T)$ after disordering the chain oxygen are shown in Fig. 2b. These conductivity spectra also have cusp-like lineshapes and $T$-linear $\tau^{-1}(T)$ characteristic of weak-limit scattering, however the widths of the spectra are significantly broadened. This broadening can only be attributed to increased quasi-particle scattering arising from disorder in the CuO chain layer. For completeness, in Fig. 2c we show $R_s(\omega, T)$ and $\sigma_1(\omega, T)$ for currents propagating in the $\hat{b}$-direction for the same YBa$_2$Cu$_3$O$_{6.50}$ sample both before and after disordering the CuO chain oxygen atoms. These data exhibit the same qualitative weak-scattering features as the $\hat{a}$-axis data.

In a $d$-wave superconductor, the linear dispersion of the energy gap sets the available phase space for quasi-particle scattering and results in a strong energy dependence of the scattering rate. For point-like defects in the limit of small scattering phase shifts, $\tau^{-1}(\epsilon) \approx 4\epsilon/\pi \Delta_0 c^2$ to within logarithmic corrections. Here $c$ is the cotangent of the scattering phase shift, $\Delta_0$ is the zero temperature superconducting gap maximum, and $\Gamma = n_i n/\pi N_0$ with $n_i$ the concentration of defects, $n$ the carrier density, and $N_0$ the density of states at the Fermi energy. In the opposite limit of large scattering phase shift, the scattering rate has a completely different energy dependence: $\tau^{-1}(\epsilon) \sim \epsilon^{-1}$. The $T$-linear spectral widths shown in Fig. 2 indicate that the scattering is closer to the weak limit where $\tau^{-1} \sim 16/\ell$. The increased slope of $\tau^{-1}(T)$ upon disordering the CuO chains indicates that the increase in the number of oxygen chain defects corresponds to an increase in the density of weak scattering defects $n_i$.

The density of oxygen chain defects can be deduced from the relationship between $T_c$ and the hole doping per Cu in the CuO$_2$ plane $p$. Using measurements of the $\hat{c}$-axis lattice parameter, Liang et al. have established this relationship empirically and found it to be close to the empirical expression of Presland et al. except near $p = 1/8$. Liang’s result gives $p = 0.093$ for the ordered sample with $T_c = 55$ K and $p = 0.084$ for the $T_c = 49$ K disordered sample. For oxygen ordered phases of YBCO with infinite chain lengths $p = p_0 \cdot y$ where $p_0 \approx 0.19$ is the maximum doping with all CuO chains filled. Away from perfect order, the number of holes contributed to the CuO$_2$ plane by a CuO chain of finite length with $\ell$ oxygen atoms is reduced by a factor of $(\ell - 1)/\ell$. Thus, if the average chain has $\ell$ oxygen atoms the doping is given by $p \approx p_0 \cdot y \cdot (\ell - 1)/\ell$. For our sample, this analysis gives $\ell \approx 24.3$ and $\ell \approx 7.6$ before and after disordering the CuO chain oxygen respectively. Considering each chain end as a scattering defect gives a defect concentration of $n_i = 0.041$ when the sample was ordered and $n_i = 0.131$ after disordering the CuO chains. Since the slope of $\tau^{-1}(T)$ in Fig. 2 nearly triples upon disordering the CuO chains, this tripling of the oxygen defect concentration suggests that CuO chain defects are the dominant source of quasi-particle scattering even in the better ordered sample.

The conductivity calculations of Hirschfeld et al. have been extended to examine the behaviour of zero frequency intercept of the conductivity spectra in the weak scattering limit. A key result of this work is:

$$\sigma_1(\omega \to 0, T) \approx \frac{1}{2} \beta_{VC} \alpha_{FL}^2 \frac{nc^2c^2}{m^* \Omega},$$

where $\beta_{VC}$ and $\alpha_{FL}$ are vertex and Fermi liquid corrections respectively. From the ordered $\hat{a}$-axis data the $\sigma_1(\omega \to 0)$ intercept is $30 \times 10^6 \Omega^{-1}$m$^{-1}$, which when combined with an estimate of $N_0 \approx 2 \times 10^{17}$ J$^{-1}$m$^{-3}$ from electronic specific heat measurements of Loram et al. gives $\beta_{VC} \alpha_{FL}^2 \approx 2.8$. It is assumed that the combination $\beta_{VC} \alpha_{FL}^2 \sim 1$, then the scattering phase shift is $\approx 30^\circ$, closer to the weak limit than it is to the large scattering phase shift limit.

There are other indications of intermediate scattering phase shifts in YBCO. Measurements of the $\hat{a}$-axis conductivity of an overdoped YBa$_2$Cu$_3$O$_{6.93}$ sample using the same broadband apparatus found that the spectra crossover from cusp-like shapes to more Lorentzian lineshapes above 4 K, indicating that this sample is best described by intermediate strength scattering. The crossover in shape occurs because impurities with intermediate scattering strength generate a resonance in the density of states. This in turn leads to deviations from $\tau^{-1}(\epsilon) \sim \epsilon$ that become important as $T$ increases. This view is also supported by recent thermal conductivity measurement.

Examining the temperature dependence of the superfluid density, $\propto \lambda^{-2}(T)$, and the normal fluid density, found by integrating $\sigma_1(\omega, T)$, tests to what extent the Ferrel-Tinkham-Glover oscillator strength sum rule is obeyed. The inset of Fig. 2 shows that, to within a constant offset, the sum rule is obeyed for the ordered $\hat{a}$-axis data. Moreover, the inset of Fig. 2b shows that, to within experimental uncertainties, the normal fluid density is independent of CuO chain order, confirming that the increased scattering caused by CuO chain disorder is not pair-breaking (note that this particular analysis is sensitive to $\lambda(0)$). The $\hat{b}$-axis analysis is complicated by an additional 1-dimensional conductivity due to the CuO chains and meaningful comparisons based upon the sum rule cannot be made.

Recent attempts by Nunner and Hirschfeld to model the conductivity of BSCCO by considering off-plane
extended scatterers have been remarkably successful. These authors were motivated by the fact that interstitial dopant oxygen atoms and cation substitution are known sources of off-plane disorder in BSCCO. The model presented in Ref. 23 led to a plausible understanding of the temperature dependence of the quasiparticle conductivity, using defect densities typical of this material. The data sets presented here are ideal for this treatment since the off-plane disorder dominates the quasiparticle transport, but unlike BSCCO this disorder is considerably smaller and can be easily manipulated in a single sample. It is particularly interesting to note that when Nunner and Hirschfeld allow for a significant forward-scattering component due to off-plane extended scatterers, they find that $\sigma_1(\omega, T \to 0)$ calculated is higher than the ‘universal’ limit obtained for point scatterers as $T \to 0$ and that this enhanced conductivity occurs over a wide frequency range. In other words, there is substantial oscillator strength in the conductivity spectrum that does not condense into superfluid as $T \to 0$. A similar phenomenon has been observed here in YBCO, where one finds a residual oscillator strength at 1.2 K that, while much smaller than that seen in BSCCO, is still larger than expected for point scatterers. Our measurements now unambiguously establish that in YBCO off-plane disorder associated with defected CuO chains provides the main source of weak quasiparticle scattering and forward scattering by these defects is the likely source of the small residual oscillator strength in YBCO. This material is particularly well suited to settling the controversial role that defects play in the physics of the cuprates since there is only one source of disorder; weakly-scattering oxygen defects that lie far from the CuO$_2$ planes.

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