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**Determination of the symmetry of the superconducting pairing state and formation
of a low-temperature normal metallic state in YBCO by electron irradiation**

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Abstract:

A key difference between a d-wave and an anisotropic s-wave superconductor is the expected effect of nonmagnetic point defects on T_c . T_c of the former becomes zero whereas T_c of the latter attains a nonzero constant value beyond a critical concentration of impurities. We report the first observation that T_c of an YBCO single crystal becomes zero after 4.1% of the planar oxygens O(2,3) are displaced by 400keV electron irradiation along the c-axis. Our data therefore indicate that YBCO is a d-wave superconductor. We also report evidence of a disorder-induced superconductor-to-normal-metal transition.

One of the most important questions regarding the copper oxide superconductors concerns the mechanism responsible for their high transition temperature. Many theories have been suggested to answer it. The most popular of these theories differ in their prediction of the symmetry of the superconducting pairing state. Some claim that the pairing state is s-wave whereas others maintain that it is d-wave. Several experimental tests of the pairing symmetry have been carried out. However, there is still no universally accepted answer.

One way to determine the nature of the pairing state is to determine the effect of *nonmagnetic* point defects on the transition temperature. For a d-wave superconductor a critical density of isotropic scattering centers will completely suppress T_c .¹ However, for an *anisotropic* s-wave superconductor T_c will initially decrease with increasing density of such centers, but it will then reach a constant nonzero value. On the other hand, the transition temperature of an *isotropic* s-wave superconductor will be affected extremely weakly by the presence of nonmagnetic defects² (Anderson's theorem).

In a previous publication³ we reported on the effect of nonmagnetic defects located in the CuO_2 planes on T_c of a high-quality detwinned single crystal of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO). The defects were induced by electron irradiation. We found that T_c is affected by small concentrations of these defects. We concluded that the symmetry of the pairing state is not isotropic s-wave, but the data could not definitely distinguish between d-wave and anisotropic s-wave. In this paper we report an investigation regarding the behavior of T_c as a function of nonmagnetic point defects up to high concentrations. We find that T_c is completely suppressed beyond a certain concentration, indicating that the symmetry of

the pairing state is d-wave. In addition, we present evidence for a disorder-induced *superconductor-to-normal-metal* transition.

The sample used in the study was a $0.7 \times 0.18 \times 0.012 \text{ mm}^3$ single crystal of YBCO grown in an yttria-stabilized zirconia crucible by using a self-flux growth technique.⁴ The crystal was configured for a-axis resistivity measurements by applying stress in the crystal's long direction during the detwinning process.⁵ This geometry guaranteed that the measured diagonal element of the resistivity tensor, ρ_{aa} , probed only the contribution of the CuO_2 planes. The dc-resistivity of the sample was measured with the four-probe technique. The low-temperature specimen stage of a High-Voltage Electron Microscope that was utilized for the irradiation provided *in situ* electrical-resistivity measurements.⁶ To avoid migration and recovery of the point defects induced by low-temperature electron irradiation, the resistivity measurements were carried out from 12K (the lowest specimen stage temperature attainable) up to 150K. The sample irradiation temperature, measured directly by monitoring the sample resistivity, varied from 90K to 120K. The energy of the electron beam, 400keV, was chosen to selectively displace only oxygen atoms. In order to get to high doses in a reasonable amount of time, we shaped the electron beam into an oblong, so that only 1/3 of the area between the voltage leads was irradiated. More details concerning the resistivity measurement and the irradiation conditions: can be found in Ref. 3.

The inset of Fig. 1 shows the raw data of resistance vs. temperature for different irradiation doses. The step at 90K, observed for all doses, corresponds to the superconducting transition of the unirradiated part of the sample located between the

voltage leads. In the main panel of Fig. 1 we plot the resistivity as a function of temperature after we subtracted the contribution of the unirradiated region. Up to a dose of $7.4 \times 10^{20} \text{ e/cm}^2$ the normal state resistivity increased and the superconducting transition temperature decreased as the irradiation dose increased. Unless the rate of T_c decrease with electron dose slows considerably, it is likely that superconductivity is totally suppressed by the electron dose of $10.32 \times 10^{20} \text{ e/cm}^2$. Beyond this dose the sample completely lost its superconducting behavior, and the resistivity exhibited a minimum followed by a plateau as the temperature decreased. The minimum in the resistivity occurred at higher temperature as the dose increased.

Fig. 2 shows the resistivity as a function of temperature upon annealing the sample to room temperature following the highest electron dose ($22.96 \times 10^{20} \text{ e/cm}^2$). Note that the resistivity decreases sharply beyond 180K. This is the temperature at which the irradiation induced oxygen defects become mobile and begin annealing, as also observed by Legris et al.⁷ Hence the reduction we observe in the resistivity comes from the elimination of some of the scattering centers. We therefore carried out our other measurements of resistivity up to only 150K. Immediately after the first anneal to room temperature, low-temperature data showed recovery in resistivity but not superconductivity, similar to the data for the unannealed sample at an electron dose of $10.32 \times 10^{20} \text{ e/cm}^2$. However, the inset of Fig. 2 shows that the sample has become superconducting again with $T_c \sim 78\text{K}$ after being stored in a dessicator for a month at room temperature. This shows that the suppression of superconductivity is indeed related to

displacements of oxygen atoms induced by the electron irradiation and *not* to some extrinsic cause such as heating of the sample that led to the loss of oxygen.

In Fig. 3a we plot the dose dependence of T_c and resistivity at 150K (well above the temperature regime where fluctuations are prominent). T_c is defined as the temperature where the resistance goes to zero. The decrease in T_c with dose is nearly linear. The increase in resistivity with dose is decidedly sublinear. In Fig. 3b we show how T_c correlates with the normalized resistivity at 150K. [$r = \rho_{15}(150K, \Phi) - \rho_{15}(150K, 0)$, where Φ is the dose. This is a way to approximate the residual resistivity]. T_c becomes zero beyond a residual resistivity of about $450 \mu\Omega\text{cm}$.

In Fig. 4 we plot the dose dependence of resistivity at 25K and 150K. For both temperatures we observe that there is a deviation from linear behavior and a tendency for saturation as we approach higher doses. The solid lines through the data points represent fits to the equation⁸

$$\rho = \rho_0 + A[1 - \exp(-\beta\Phi)] \quad (1)$$

where ρ_0 , A and β are fitting parameters. Eq. (1) describes the phenomenon known as spontaneous recombination of point defects. The values of the fitting parameters are shown in Fig. 4. Note that the value of β , which is related to the effective volume for the athermal capture of a displaced atom by a vacancy, V_e , is very similar for the two temperatures. Simple theoretical arguments can relate β to $2V_e\sigma_d$ and A to $\rho_d/2V_e$, where σ_d is the cross section for displacing an atom and ρ_d is the resistivity per defect.⁹ This yields an average spontaneous recombination volume for the O(2) and O(3) sites of 5.5 atomic volumes, a quite reasonable value for this complex structure in comparison to the

much larger value of 125 atomic volumes for the close packed metal Cu.⁹ The fact that the resistivities at 25 and 150K have the same functional dependence on dose suggests that there is no change in the charge carrier density between the two temperatures with increasing defect concentration. However, the value of A at 25K is about twice that at 150K suggesting a strong temperature dependence of the resistivity per defect.

In an earlier publication¹⁰ we reported that the minimum electron energy to displace Cu atoms is $400 < E_{\min} \leq 600\text{keV}$ for electron irradiation perpendicular to the CuO_2 planes. Hence, we expect the low-temperature irradiation with 400keV electrons to produce isolated interstitial-vacancy pairs by displacing *only* oxygen atoms from all crystallo-graphic positions, i.e., planar [O(2,3)], basal [O(1)] and apical [O(4)] oxygens. By measuring the ρ_{aa} component of the resistivity tensor (the resistivity along a-axis, perpendicular to the direction of the chains) we probed the contribution of the scattering by the planar oxygen vacancies to the resistivity. The concentration of these vacancies can be calculated by using the expression:

$$C = \sigma_d \Phi \quad (2)$$

where σ_d is the cross section to produce an oxygen atom displacement. To calculate the planar oxygen vacancy concentration for a given dose we have used Eq. (2) taking values of the cross section for displacement from Ref. 11 of 58.8 barns for the O(2) site and 21.4 barns for the O(3) site, assuming threshold displacement energies of 10eV on the O(2) site and 20eV on the O(3) site. The lower threshold has been measured experimentally by Legris et al.⁷ and Tolpygo et al.¹² and found to be in agreement with the calculations of Kirsanov et al.¹³ The upper threshold energy for the O(3) site is taken from the same

calculations of Kirsanov et al. Threshold recoil energies near 20eV, measured by Basu et al.¹⁴ and Kirk et al.¹⁵ are specific to the O(1) chain site and the irradiation directions used in their experiments. Using the above values for the two cross sections, taking the average to reflect the vacancy concentration on both sites, gives a value of 4.1% for the planar oxygen vacancy concentration for an electron dose of 10.32×10^{20} e/cm² at which T_c becomes zero. For this vacancy concentration, the average distance in the plane between vacancies is 1.34nm.

For this calculation to correctly give the concentration of O(2) and O(3) vacancies, the induced defects must be frozen in the lattice. This requirement was satisfied by irradiating at low temperatures (sample reached a maximum temperature of 120K during irradiation) and measuring the resistance of the sample up to a maximum temperature of 150K.

The irradiation-induced defects are *not* magnetic according to the unpublished work by Welp¹⁶. In their study they measured the normal state susceptibility of a large YBCO single crystal before and after irradiation with 1MeV electrons to relatively low doses. They found no evidence for a Curie-Weiss tail. Hall effect measurements by Legris et al.⁷ of YBCO single crystals as a function of electron irradiation dose (under conditions similar to the ones used by us) have shown that the carrier concentration remains unaffected by the induced disorder. Preliminary infrared reflectivity measurements by Giapintzakis et al.¹⁷ of a YBCO crystal before and after irradiation with 1MeV electrons to low doses have shown that the plasma frequency also remains unaffected by the induced disorder. Therefore, by irradiating with 400keV electrons we

have introduced nonmagnetic defects on the CuO_2 planes without affecting the carrier concentration or the plasma frequency.

A main difference between an anisotropic s-wave superconductor and a d-wave one is the way T_c is affected by disorder. T_c becomes a non-zero positive constant for the first and zero for the second kind beyond some characteristic density of nonmagnetic impurities. Our data (Fig. 3a) show clearly that $T_c = 0$ when 4.1% of the planar oxygens are displaced. The solid line through the data points in Fig. 3b is a fit to the depairing function for a d-wave superconductor with isotropic nonmagnetic impurity scattering:¹

$$\ln\left(\frac{T_c}{T_{co}}\right) = \Psi\left(\frac{1}{2}\right) - \Psi\left(\frac{1}{2} + \frac{\alpha T_{co}}{2\pi T_c}\right) \quad (3)$$

where $\Psi(x)$ is the digamma function and α is the strong-coupling pair-breaking parameter.

Radtke et al.¹ have been able to express α in terms of the planar resistivity ρ_o :

$$\rho_o \cong \frac{4\pi}{\omega_{pl}^2} 2T_{co}\alpha \quad (4)$$

where ω_{pl}^* is the renormalized plasma frequency. Using our experimental values for T_{co} , T_c and ρ_o we obtained the best fitting for $\omega_{pl}^* = 0.47$ eV. This value of the plasma frequency for the CuO_2 planes is about a factor of 2 less than the value determined by other experimental techniques, such as infrared reflectivity.¹⁸ A possible explanation for this discrepancy may be that the impurity scattering is not isotropic as we have assumed, but it involves other channels in addition to s-channel.

In light of the disorder-induced suppression of the superconductivity an interesting question arises concerning the electronic state of the system, i.e., is the system still metallic or does it become insulating? If disorder drives the system to an insulating phase,

we would expect the low-temperature resistivity to increase exponentially as a function of both temperature and dose. However, this is not what we have observed. As seen in Fig. 1 the resistivity exhibits a minimum followed by a plateau below 20K. In addition, the resistivity at 25 K shows a tendency to saturate and has the same dose dependence [Eq. (1)] as the resistivity at 150K, which is metallic. Based on these arguments we suggest that the system remains metallic following the suppression of the superconductivity. Therefore, electron irradiation provides a way to quench superconductivity and access the normal state at low temperatures in YBCO₇ single crystals while they retain their structure and a rather small fraction of the O(2) and O(3) oxygen atom sites are vacant.

Previous light-ion irradiation experiments on thin films have observed an exponential increase in induced resistivity with irradiation dose. All authors have interpreted this as evidence for a disorder induced metal-to-insulator transition.^{19,20} It is likely they were all observing effects of structural phase changes with irradiation²¹ and not the simple defect resistivity behavior in a metal as in the present experiment.

In conclusion, we measured the temperature dependence of a-axis resistivity of YBCO as a function of dose for 400keV electron irradiation. We have found that the superconductivity is completely suppressed beyond a critical dose that displaces 4.1 % of all planar oxygens. The loss of superconductivity by the irradiation-induced nonmagnetic defects has been interpreted as evidence that the symmetry of the pairing state is d-wave. In addition, we have presented evidence that the disorder induces a superconductor-to-normal-metal transition.

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Figure Captions:

FIG. 1. (Main panel) The temperature dependence of the resistivity ρ_{xx} for different electron irradiation doses after subtracting the contribution of the unirradiated part of the crystal between the voltage leads. The inset shows the raw data of resistance versus temperature for the same electron doses.

FIG. 2. (Main panel) The temperature dependence of the resistivity ρ_{xx} up to room temperature following electron irradiation to a dose of $2.3 \times 10^{22} \text{ e/cm}^2$. Note that beyond $T=180\text{K}$ ρ_{xx} decreases drastically. The inset shows the temperature dependence of the resistance after storing the irradiated sample in a dessicator at room temperature for a month. Note that the crystal becomes again superconducting with $T_c \sim 78\text{K}$.

FIG. 3. (a) The dose dependence of T_c (filled symbols) and normalized resistivity $r(150\text{K})$ (open symbols). (b) T_c versus r at 150K . The solid line through the data points is a fit to Eq. (3).

FIG. 4. The dose dependence of the resistivity at 25K and 150K . The solid lines going through the data points are fits to Eq. (1).

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FIG. 1

FIG. 2

FIG. 3

FIG. 4