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# NORMAL STATE A.C. CONDUCTIVITY OF $YBa_2Cu_3O_{7-\delta}$

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We have measured the a.c. conductivity of fully oxygenated and oxygen deficient polycrystalline and single crystal Y-Ba-Cu-O samples. We find no evidence for a frequency dependent conductivity in the frequency range d.c. to 1 GHz. We also measured the dielectric constant K for oxygen deficient samples. While the single crystal shows a low K, the polycrystalline samples show a very large K (K≈600), which we ascribe to capacitive coupling between grains.

## 1. Introduction

The transport and superconducting properties of the Cu - O based high temperature superconductors are highly anisotropic[1,2,3]. For example, the resistivity of $YBa_2Cu_3O_{7-\delta}$ (YBCO) crystals is substantially higher along the c axis (orthogonal to the Cu - O planes) than along the a-b plane, $\rho_c/\rho_{ab}$ ≈30-100 [1,4] at room temperature. Moreover, for many crystals the temperature dependence of the resistivity is qualitatively different between the two directions; whereas the a-b plane shows a positive, metallic temperature coefficient ($dR/dT > 0$), the c axis resistance shows little temperature dependence down to T ~ 150K below which a "semiconductor-like" upturn in resistance is seen ($dR/dT < 0$). For some crystals, on the other hand, the "upturn" in the c axis resistivity starts only very close to $T_c$ [4,5], or is not seen[6]. The difference may be a combination of impurities (including oxygen vacancies) and degree of twinning in the a-b plane. For any crystal the upturn is easily enhanced by depleting the oxygen content. The qualitative difference in the conductivity between the a-b and c directions suggests that two different conduction mechanisms may be operating in the two directions. While the a-b plane shows metallic resistivity, the origin of the c axis conductivity is still controversial.

Determination of the a.c. conductivity in the high $T_c$ materials can be used in deciding on mechanisms and models. One of the hallmarks of hopping conductivity in systems with localized electron states is a frequency dependent a.c. conductivity[7]. An electron hopping between two localized states can give a contribution to the a.c. conductivity: when the frequency dependent a.c. hopping length becomes comparable or smaller than the d.c. hopping length the a.c. conductivity starts exceeding the d.c. conductivity. The typical behavior seen in disordered semiconductors is $\sigma(\omega) \propto \omega^s$ (s~0.8) where the frequency dependence develops in the $\omega$ ~ $10^6$ - $10^7$ Hz range at room temperature and well below that at lower temperatures. Both metals and semiconductors also show frequency dependent a.c. conductivities but at much higher frequencies. For metals the characteristic energy is $\omega\tau$ ~1 (or $\omega$ ~ $10^{14}$ Hz) while for semiconductors it is $h\omega/2\pi$ ~ 2 $\varepsilon_g$. Previously published work seems to indicate that there might be some interesting frequency effects in the high $T_c$ materials and their related compounds. Measurements on single crystal $Eu_2CuO_4$ showed a frequency dependent complex conductivity in the GHz frequency range[8]. Furthermore, it was found that an insulating, high temperature quenched phase of polycrystalline YBCO exhibited a large dielectric constant[9]. The polarizability of the material could imply a frequency dependent a.c. conductivity.

We have performed a.c. conductivity measurements on polycrystalline and single crystal YBCO in order to shed more light on the question of the conductivity mechanisms operating in these systems. We have performed measurements in the frequency range d.c. up to 1 GHz and in the temperature range of room temperature down to below the superconducting transition. For polycrystalline YBCO we find the absence of a frequency dependence to the conductivity for fully oxygenated samples up to 200 MHz and for oxygen deficient samples up to 1 MHz. In oxygen deficient samples we measure a large dielectric constant, K ≈ 100 - 600, which we ascribe to the presence of capacitances formed at grain boundaries. We have measured fully oxygenated and oxygen deficient crystals in the c axis and the a-b plane directions up to 1GHz. We find no frequency dependence in the a.c. conductivity, i.e. $\sigma(\omega) = \sigma_{dc}$. The dielectric constant of an oxygen deficient single crystal measured along the c axis is K ≈ 10.

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## 2. Experimental Detail

The a.c. resistivity measurements were made using network analyzers, HP instruments number 8754 (range 1-1300 MHz) and 4192A (5Hz - 10MHz). For the high frequency measurements the samples were mounted in a two probe configuration and formed the termination of a microcoaxial cable serving as a transmission line. A sinusoidal signal is sent down the transmission line and from the amplitude and phase of the reflected signal the admittance $Y(\omega)$ of the sample is calculated. Since we model the sample as a resistor in parallel with a reactive component (capacitor or inductor), the admittance is related to the resistance R and susceptance B via the relation $Y(\omega) = 1/R(\omega) + iB(\omega)$. If the reactive component is a capacitor then $B(\omega) = \omega C$, where C is the capacitance. In this communication we report on the real part of the impedance, $R(\omega)$, and compare it to $R_{dc}$. Measurement of the dielectric constant (or equivalently the imaginary part of the admittance) was not possible for these very highly conducting samples, since this involves measuring a capacitance in parallel with essentially a short circuit. The low frequency instrument allows for four probe measurements. Oxygen deficient polycrystalline samples have contact resistances that are frequency dependent and they were thus measured in a four probe configuration on the low frequency instrument up to 1MHz only.

The dielectric constant of oxygen deficient samples was determined by inserting the samples between capacitor plates. The dielectric constant K was obtained from the capacitance through the relation $C = \varepsilon_o KA/d$, where $A \approx 1\ mm^2$ is the area of the plates, d the distance between plates and $\varepsilon_o$ the electric permittivity of free space. The measurement was calibrated by using insulating materials of known dielectric constant. The capacitances measured were on the order of 1 pF and were measured at the frequency $\omega/2\pi = 100kHz$ using the HP4192A network analyzer.

The single crystal YBCO samples used for this study were grown by slow cooling a non-stoichiometric melt in a gold crucible. Electrical contact was made by painting gold wires onto the sample with silver paint and subsequently annealing in an oxygen atmosphere. This procedure gave pristine oxygen (PO) samples. These samples showed the onset of superconductivity at temperatures, $T_c$, between 88K and 91K and had transition widths of around 2K. Oxygen deficient (OD) single crystalline samples were prepared by placing PO samples in a rough vacuum at a temperature of 500°C for 1 hour or longer. Specifically, the sample corresponding to the data of Fig. 1(b) was annealed for one hour, the sample of Fig. 2(a) for 5 hours and the sample of Fig. 2(b) for 15 hours. This procedure reduced $T_c$, smeared the transitions, and resulted in a deterioration of the contacts. While the contact resistance to PO samples is typically $0.2\Omega$, the contact resistance to OD samples was $0.4\text{-}3\Omega$.[10]

The large single crystal used for the measurement of the dielectric constant was from a different growth batch and had dimensions of 1mm x 1mm x .08mm. Prior to depleting the oxygen content of the sample, it had a $T_c$ onset of 78K and a width of 10K. The sample was annealed in vacuum at 600 °C for 6 hours before K was determined.

The polycrystalline samples were made by the usual solid-state reaction technique. We prepared three different OD polycrystalline samples (A, B, and C). Sample A and B were of the same batch. Sample A was quenched from 800 °C after 17 hours of annealing at that temperature in flowing oxygen. The room temperature resistivity of sample A was $\rho \approx 0.03\ \Omega cm$ after the anneal. Sample B, starting out as a fully oxygenated sample, was annealed in vacuum for 1 hour at 500°C and had a room temperature resistivity of $\rho \approx 6\Omega cm$. Sample C was from a different, more porous and more brittle batch. It was prepared by annealing in vacuum at 600°C for 1 hour. Conductivity measurements were made on samples A and B. The dielectric constants of samples A and C were measured.

## 3. Results and Discussion

First we present our experimental results on the polycrystalline YBCO. We measured the a.c. and d.c. resistivity of PO YBCO at 200 MHz and found $\rho_{ac} = \rho_{dc}$ for all temperatures from RT down to 40K. We also measured OD samples, sample A ($\rho = 0.03\Omega cm$) and sample B ($\rho = 6\Omega cm$) as described in section 2. Both samples were measured in a four probe configuration from 0 to $10^6$ Hz and showed no frequency dependence in their resistivities. Sample A was measured at different temperatures from RT down to 20K while sample B was measured at RT only. The dielectric constant was measured for samples A and C. For sample A we obtain a value $K \approx 600$ while for sample C we obtain $K \approx 100$. These values differ greatly, and this could be due to different oxygen concentrations and/or because of the different densities/porosities (sample A was pressed into a pellet at three times the pressure as used for sample C). What is, however, obvious is that OD polycrystalline YBCO has a very large dielectric constant. Our values for K are comparable to those determined by Testardi et al.[9], who found $K \approx 700$ for a polycrystalline YBCO sample quenched from around 900 °C.

In order to determine if the large dielectric constant measured for the OD polycrystalline YBCO is intrinsic to the YBCO material or is due to grain boundary effects we measured the dielectric constant of an OD single crystal. This sample filled the space between capacitor plates. At room temperature we found $K \approx 10$ along the c axis. This value for the dielectric constant of an OD YBCO crystal is not unusually large, and this suggests that the large K measured for OD polycrystalline YBCO is due to the granular nature of the material. The situation for OD polycrystalline YBCO may be analogous to thin films near percolation threshold, where large dielectric constants are measured[11,12].

Next we will present and discuss our results on the a.c. conductivity of crystalline YBCO. This measurement is of interest since it can serve to further characterize the c axis conductivity. If conventional localization is responsible for the "semiconductor-like"

behavior of the c axis resistivity then one might observe frequency dependence in the resistivity.

In Fig. 1(a) we compare the temperature dependence of the d.c. and a.c. resistance (measured at 14 MHz) of a c axis PO sample. At room temperature $R_{dc}$ = 0.4Ω; of this value ~0.25 Ω can be attributed to contact resistance. The sample shows the characteristic upturn in resistance as a function of decreasing T. This data shows no difference between the a.c. and d.c. resistance. We have measured the a.c. resistance for other samples up to a frequency of 100 MHz and did not see evidence for any deviation of the a.c. from the d.c. c axis resistivity. In Fig. 1(b) we show R vs. T for an OD sample measured in the c direction. The $T_c$ has been reduced to ~ 60 K and the temperature dependence of the resistivity has changed. The ratio of the resistance near $T_c$ to the resistance near 300K is now $R(T_c)/R(300K)$~2.5, whereas for the PO sample $R(T_c)/R(300K)$~1.3. This measurement is made at 1 GHz and again the a.c. and d.c. measurements agree, showing the absence of a frequency dependence to the a.c. c axis conductivity. These figures show raw data. There is an offset between the d.c. and a.c. measurements which is due to calibration error. The temperature dependences, however, which are the subject of our interest are not affected by this error.

In Fig. 2(a) and (b) we show the resistance as a function of temperature for two OD samples along the a-b plane taken at 1 GHz. The sample of Fig. 2(a) is more OD than the sample of (b). Again, within calibration error, the a.c. and d.c. resistances agree in both samples, ruling out a frequency dependence of the a.c. a-b plane resistivity up to 1GHz. Note that the resistance in Fig. 2(b) shows an upturn as a function of decreasing temperature just above $T_c$ which shows up in the d.c. and a.c. measurements. The sample of Fig. 2(a) has a broad resistive transition centered around $T_c$ ~ 60K. Of the 1.4 Ω measured at room temperature, ~1Ω is due to the sample and ~0.4Ω due to contact resistance. The sample of Fig. 2(b) has a $T_c$ of around 40K, a resistance of ~3.75Ω with a contact resistance of ~2.75Ω. The drop of the a.c. resistance below the d.c. resistance for $T<T_c$, which is seen in Fig.'s 1(b) and 2(a), is probably due to a frequency dependence of the contact resistance below $T_c$.

In short, our experiments on the a.c. c axis and a-b plane resistivities of YBCO show no anomalous frequency dependence below 1GHz. This suggests that interpreting the "upturn" in the c axis resistivity in terms of conventional models of hopping or localization may not be appropriate. This conclusion was also arrived at by Hagen et al.[4] who argue against localization based on the absence of significant disorder in the c direction as determined by Laue diffraction. Another possible explanation for the c axis resistivity behavior is in terms of activated behavior as in a semiconductor. Measurements [5,13,14] on the thermopower S of YBCO, however, do not agree with this interpretation, since $S_c$ for YBCO shows a linear decrease with T from 300K down to $T_c$ (whereas the thermopower of a semiconductor should be inversely proportional to the temperature, $S \propto 1/T$).[15]

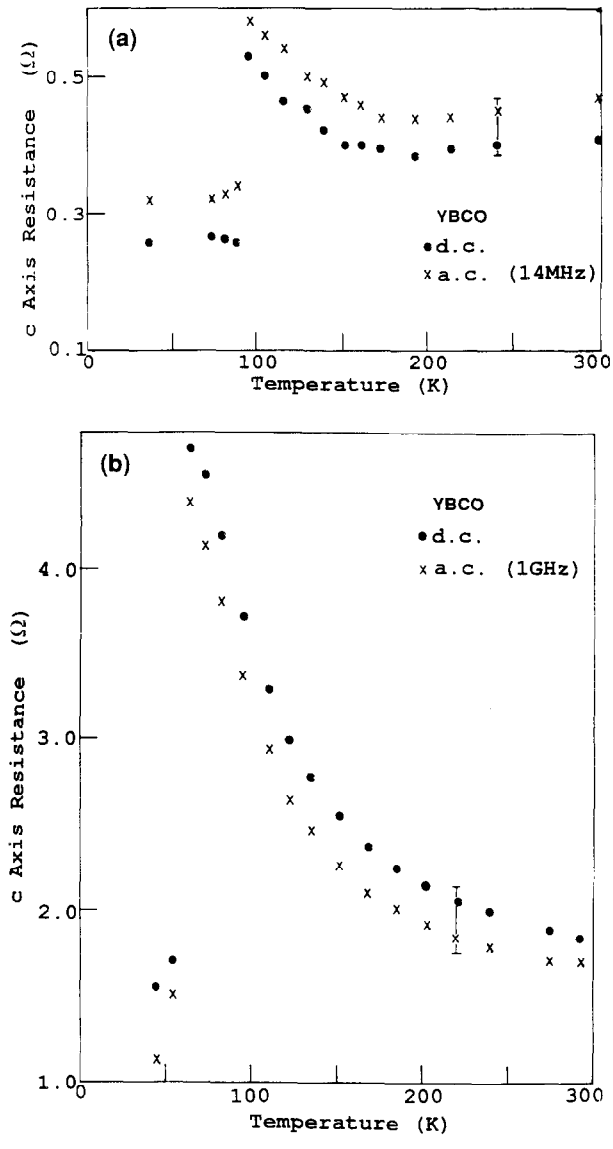


Fig.1 Comparison between the a.c. and d.c. resistance of YBCO crystals along the c axis. (a) shows a fully oxygenated sample ($\omega/2\pi$ = 14 MHz) and (b) corresponds to an oxygen deficient sample ($\omega/2\pi$ = 1GHz). Within instrument calibration error, no frequency dependence is observed in the normal state resistance.

Our results may have consequences for relevant energy scales within other models proposed for the high $T_c$ materials, in particular models that rely on defect states or localization and hopping conductivity. Doniach et al.[16] suggest a model in which the charge carriers are bosons of charge |2e| (Cooper pairs) but which lack long-range coherence above the "zero resistance transition" temperature due to localization of these carriers. Another example is the defect assisted percolation model proposed by Phillips[17]. Although frequency

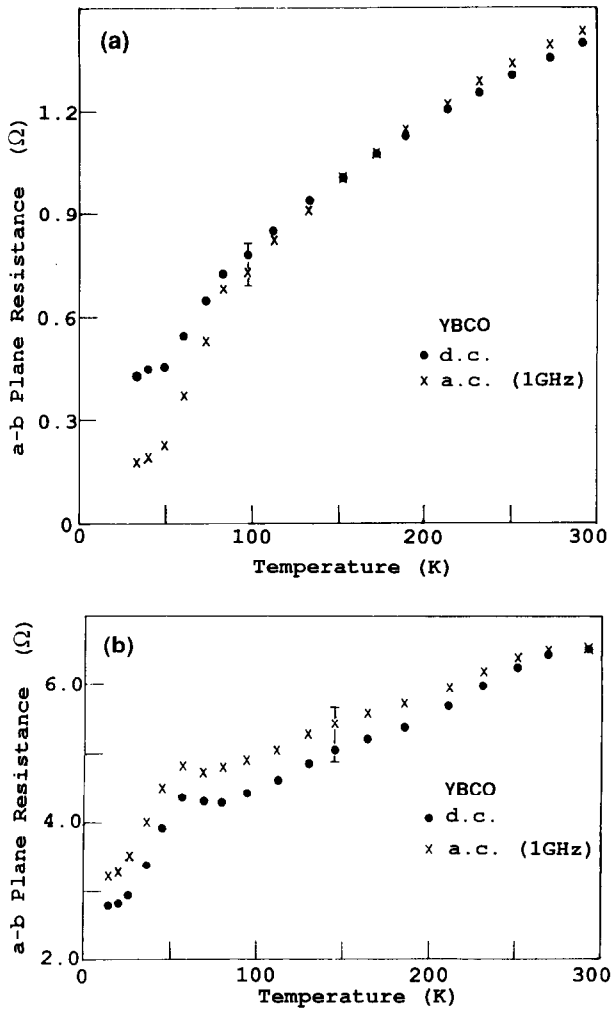


Fig.2 A.C. ($\omega/2\pi$=1GHz) and d.c. resistance of YBCO crystals in the a-b plane. Both (a) and (b) show oxygen deficient samples. $R_{dc}$ agrees with $R_{ac}$ in the normal state.

dependent conductivity may be a consequence of such mechanisms[18], our experiment suggests a characteristic frequency greater than 1 GHz. It is interesting to note, however, that measurements[19] on the related non-superconducting material $La_2CuO_4$ showed that for single crystals the resistivity had a temperature dependence characteristic of hopping conductivity, i.e. $\ln\rho \sim (T_o/T)^{1/4}$. A later study[20] on the same material found hopping conductivity at low T but diffusive transport at higher temperatures.

Our results appear consistent with measurements by Ho et al.[21] They measured the complex conductivity of BiCaSrCuO superconducting thin films at $\omega$ = 60 GHz and report a dielectric constant of ~10 at room temperature and a frequency independent conductivity, i.e. $\sigma_{dc} = \sigma(\omega=60GHz)$. This indicates that a frequency independent conductivity and a low dielectric constant may be a common feature of all Cu-O based superconductors.

In conclusion, we have measured the dielectric constant K of oxygen deficient YBCO. For single crystals we find K ~10 in the c direction, which points out that the Cu-O planes are not highly polarizable in the c direction (at least not in the oxygen deficient state). For polycrystalline YBCO we find a large K which we attribute to capacitive coupling between the grains. We also measured the a.c. conductivities of fully oxygenated and oxygen deficient single crystalline and polycrystalline YBCO. We find no evidence for a frequency dependent conductivity in the low energy range d.c. to 1 GHz.

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