EDDY CURRENT SENSING OF OXYGEN CONTENT IN HIGH-T\textsubscript{c} SUPERCONDUCTORS

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INTRODUCTION

The superconducting properties of Ba\textsubscript{2}YCu\textsubscript{3}O\textsubscript{7-x} are strongly dependent on the amount of oxygen contained in the material. Although the physical mechanisms of oxidation have not yet been fully characterized, the reaction rates appear to be influenced by surface adsorption, in addition to bulk diffusion [1,2]. The task of constructing an optimal high-temperature processing schedule is, therefore, complicated by the fact that porosity and surface conditions strongly influence oxidation. An additional complication arises from the fact that, while the diffusion and adsorption rates increase with increasing temperature, the equilibrium oxygen concentration in the material decreases with increasing temperature, so that, after the final annealing, cooling must proceed slowly enough to allow adequate absorption to occur.

This situation suggests a need for sensors which can monitor oxygen content during high-temperature processing of Ba\textsubscript{2}YCu\textsubscript{3}O\textsubscript{7-x}. The most obvious basis for such a sensor is, perhaps, the normal state resistivity, which is greatly influenced by the number of carriers contributed by the oxygen. Flory, et al., [3] find that the resistivity increases roughly one order of magnitude as x is changed from 0 to 1 at 600°C. This effect has been used as a means of studying the kinetics of oxygen diffusion and adsorption using a four-point contact technique [1].

In this report, we describe a non-contact eddy current technique for measuring resistivity. A sensor has been designed and tested on model silicon samples at room temperature. Changes in the impedance of the sensor with a Ba\textsubscript{2}YCu\textsubscript{3}O\textsubscript{7-x} sample inserted have been monitored at elevated temperatures as the atmosphere around the sample is varied.

SENSOR DESIGN

A schematic diagram of the eddy current sensor is shown in Figure 1. A small coil, with inductance L, surrounds the sample and is connected in parallel with a capacitor, C. The sample is in the shape of a short

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solid cylinder, a typical geometry used for research on high-\(T_c\) mate-
rials. A Hewlett Packard 9194A impedance analyzer is used to measure the
impedance of the circuit. With the coil empty, the circuit has a paral-
lel resonant frequency, \(\omega_0\), near \((LC)^{-1/2}\), where the magnitude of the
impedance reaches a maximum. Losses in the empty coil and capacitor are
best modeled by resistors, \(R_L\) and \(R_C\), in series with each of these
components, respectively. The empty coil impedance at resonance is given by

\[
Z_e = \frac{L + CR_L R_C}{C(R_L + R_C)}
\]

(1)

(the imaginary part being zero), where both \(R_L\) and \(R_C\) are assumed to be
much less than \(\omega_0 L\) and \(1/\omega_0 C\).

With the sample inside the coil, eddy current losses cause the
impedance at resonance to be reduced. In order to provide an expression
for the sample resistivity, \(\rho\), in terms of the circuit impedance, we
proceed by assuming that the electromagnetic skin depth is much larger
than the sample dimensions, so that the magnetic field is essentially
unchanged by the presence of the sample. We also approximate the magneti-
c field as pointing along the axis of the coil with a constant amplitude
throughout the sample. The electric field is, then, oriented along the
azimuthal direction, with an amplitude given by

\[
E = \frac{1}{2} \omega_0 \mu_0 H r
\]

(2)

where \(H\) is the amplitude of the magnetic field and \(r\) is the distance from
the coil axis. The time-averaged power loss, \(P_S\), in the sample is found
by integrating resistive losses over the volume of the sample:

\[
P_S = \int \frac{1}{2 \rho} E^2 dV \equiv \frac{\pi b}{16 \rho} (\omega \mu_0 H a^2)^2
\]

(3)

where \(a\) and \(b\) are the radius and length of the sample, respectively, and
the axis of the sample lies along the coil axis. We take \(H\) to be its
exact value at the center of the empty coil [4]:

\[
H = \frac{nI}{[1+(d/h)^2]^{1/2}}
\]

(4)

![Fig. 1: Schematic diagram of the eddy current sensor.](image-url)
where \( n \) is the number of turns per unit length, \( d \) is the coil diameter, \( h \) is the coil length, and \( I \) is the amplitude of the current passing through the coil.

Since \( P_s \) is proportional to \( I^2 \), the effect of the sample can be modeled by an additional resistor, \( R_s \), in series with the inductor:

\[
R_s \approx \frac{\pi b (\omega_0 \mu_0 n a^2)^2}{8 \rho [1 + (d/h)^2]}
\]  \( (5) \)

and the impedance at resonance becomes

\[
Z \approx \frac{L + C (R_L + R_S) R_C}{C (R_L + R_S + R_C)}
\]  \( (6) \)

We have selected circuit elements such that \( L \gg C (R_L + R_S) R_C \), which leads, from Equations 1, 5, and 6, to a simple approximate expression for the resistivity of the sample:

\[
\rho \approx \left[ \frac{1}{Z} - \frac{1}{Z_0} \right]^{-1} \frac{(\omega_0 \mu_0 n a^2)^2}{8 L [1 + (d/h)^2]} \pi C b
\]  \( (7) \)

EXPERIMENTAL RESULTS

Device testing at room temperature

To facilitate tests at room temperature, a sensor was constructed from a coil with a diameter of 2.0 cm, a length of 7.4 cm, and an inductance of 10.4 \( \mu \)H. A 2.7 nF capacitor was connected in parallel, giving a resonance near 947 kHz. Two phosphorus-doped silicon samples with known resistivities of 0.26 \( \Omega \)-cm and 0.71 \( \Omega \)-cm (as determined by four-point measurements) were used to determine the accuracy of the measurement technique. These samples are in the shape of solid cylinders, with a radius of 0.67 cm and a length of 0.62 cm. The resistivities are comparable to the highest values expected during high-temperature processing of \( \text{Ba}_2\text{YCu}_3\text{O}_{7-x} \) [1,5].

Figure 2 shows room-temperature measurements of the sensor impedance as a function of frequency with the coil empty and with each of the two silicon samples inserted. Applying Equation 7 to the values of \( Z \) at resonance, we calculate resistivities of 0.74 \( \Omega \)-cm and 0.28 \( \Omega \)-cm for the two silicon samples which were determined by the four-point method to have resistivities of 0.71 \( \Omega \)-cm and 0.26 \( \Omega \)-cm, respectively. We consider this to be a good result, considering the approximations involved in the calculation. It should be noted that the skin depth, \( \delta \), is 2.6-4.4 cm for these samples (4-7 times the sample radius), so that the approximation \( \delta \gg a \) is not very accurate. One expects, in this situation, that measured values of \( \rho \) will be a few percent high as a result of the magnetic field in the sample being lower than the empty coil value which has been assumed in Equation 4. The calculation can be made more accurate by employing a more elaborate mathematical model. It can not, on the other hand, be easily made more accurate by reducing the frequency. Although \( \delta \) varies as \( \omega^{-1/2} \), the relative drop in \( 1/Z \) induced by the presence of the sample is proportional to \( \omega^2 \), making the device much less sensitive at lower frequencies.
High-temperature measurements

Measurements at 400–800°C were performed with the aim of demonstrating the sensitivity of the device to changes in oxygen content in Ba$_2$YC$_2$O$_{7-x}$ at processing temperatures. No attempt was made to obtain quantitative values of sample resistivity, which would require separate measurements of the empty coil impedance as a function of temperature and, also, may necessitate switching the capacitor to accommodate varying ranges of $\rho$. A platinum-wound coil was employed at a relatively high resonant frequency, 2.3 MHz, in order to provide greater sensitivity in the measurement. The sample used in the measurements was a sintered pellet of Ba$_2$YC$_2$O$_{7-x}$ with ~25% volume fraction of pores and an initial value of $x$ near 0 (this having been deduced from the fact that magnetic susceptibility measurements indicate a $T_c$ near 91K). The sample was produced from Y$_2$O$_3$, BaCO$_3$, and CuO powders by the solid state reaction technique which has been described elsewhere [6].

Figure 3 shows measured changes in $Z$ at resonance as a function of the atmosphere surrounding the Ba$_2$YC$_2$O$_{7-x}$ at 790°C. After the sample had been heated in flowing air to this temperature, flowing argon was introduced into the furnace chamber, followed by repeated cycling of air, argon, and oxygen. The data demonstrate the reproducible changes in $Z$ which occur as the sample gains and loses oxygen. The fact that $Z$ decreases with increasing oxygen content is consistent with previously published four-point resistivity results [1,3,5]. The time constants for equilibration shown in this figure are on the order of a couple of minutes, or less, (somewhat slower for the switch from air to argon) and may reflect the rate with which gas is purged from the furnace chamber, rather than the kinetics of oxygen absorption and desorption in the sample.

Fig. 2: Eddy current sensor impedance as a function of frequency near resonance with no sample inside the coil and with two silicon samples having resistivities of 0.26 Ω-cm and 0.71 Ω-cm.
Fig. 3: Sensor impedance at 790°C with a Ba$_2$YCu$_3$O$_{7-x}$ sample, as the atmosphere is cycled between air, argon, and oxygen.

Fig. 4: Sensor impedance at 435°C with a Ba$_2$YCu$_3$O$_{7-x}$ sample, as the atmosphere is changed from air to argon and, then, back to air. A brief rough pumping was performed before introducing argon.
Measurements at 435°C (Figure 4) show an approach to equilibrium which takes place much more slowly than at 790°C. Having established approximate upper limits for gas exchange time constants from the measurements at 790°C, we attribute the slowing of the process at 435°C to kinetics within the sample. The decaying curve in Figure 4, which corresponds to oxygen being gained by the sample, is roughly fit by an exponential with a time constant of 1300 seconds, not inconsistent with previously published results [1,2]. (An exact comparison is not possible, since the rate depends on porosity and the degree of oxygenation of the sample). Oxygen loss (in argon) proceeds more slowly than oxygen gain, as it did at 790°C. This behavior has also been observed by other workers, and is explained by surface desorption being the rate-limiting process as oxygen leaves the sample [1].

CONCLUSION

The expected changes in resistivity produced by varying the atmosphere surrounding the sample at elevated temperatures are easily detected using the eddy current sensor. Because of the strong dependence of the resistivity on the oxygen content, the sensor appears to be useful as a materials research tool in its present form, using the approximate equations which we have presented. The simplicity of the device would allow it to be easily incorporated into most existing furnaces used for processing high-Tc materials.

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