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Juana Vivó Acrivos
San Jose State University, juana.acrivos@sjsu.edu

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Electrochemistry of YBa2Cu307-d above Tc and rf Dissipation below Tc

Juana Vivó Acrivos, *San Jose State University*
R. Ithnin
C. Bustillo
M. Chen Lei
D. Ptak

ELECTROCHEMISTRY OF $YBa_2Cu_3O_{7-\delta}$ ABOVE T_c AND RF DISSIPATION BELOW T_c

J.V. Acrivos, C. Bustillo, M. Chen Lei and D. Ptak
San Jose' State University, San Jose' CA 95192

Abstract: New experiments that characterize high T_c superconducting materials from the classical electrochemistry to the bulk quantized states are described.

INTRODUCTION

The disorder present in Type II superconducting perovskites (e.g., $Y_1Ba_2Cu_3O_{7-\delta,\delta\to 0}$, or 1:2:3 and, the Tl and Bi derivatives)[1] can be determined by electrochemical measurements in the range $298 > T > 150\ K > T_c \approx 92\ K$. For example in: Cu| Cu^{2+} bridge |1:2:3|Pt|Cu, in the absence of chemical attack on the superconductor, the cell reaction is:[2]

$$1/2\ Cu(metal) = 1/2\ Cu^{2+}(1:2:3) + e^-(1:2:3). \qquad (1)$$

Also, the induction signal produced in the direction normal to the applied fields, at 77 K < T_c, by superconducting lamellae (oriented and isolated in an epoxy matrix) subject to an rf field $H_x = 2H_1 \sin wt$ at $w/2\pi = 8.00$ MHz **versus** a field $H_z + H_{mz}$ ($H_z = \pm 20$ Oe and $H_{mz} = 2H_m \sin w_m t$ at $w_m/2\pi = 1.56$ kHz) gives a physical insight into the energy levels for the superconducting electron pairs moving in lamellae isolated in an epoxy matrix in Figure 1.[2] These dissipation signals describe the ground state of the superconductor as free particles moving in a ring around normal metal areas of several μm^2. In the presence of Josephson junctions a potential V mixes states for the particle in a ring with different quantum number m in Figure 2a to give the ground state energy.

The dissipation signal when H_1, $H_m < 0.05$ Oe (critical H_{c1}) can be interpreted for the lamellae, in Figure 1, as shown in Figure 2.[2] In the presence of Josephson junctions the flux in units of the quantum of flux $\Phi_0 = 2.067 * 10^{-15}$ Wb is:[2]

$$f = f_e - f_s \sin(2\pi f). \tag{2}$$

$f_s = Li/\Phi_0$; L is the self inductance and i is the critical current in the cylinder; the external flux $f_e = \mathbf{H} \cdot \mathbf{n}_0 O/\Phi_0$ (O is the area and $\mathbf{n}_0$ is its unit normal in Figure 1). When $df/df_e \to \infty$, the induced emf (df/dt) gives rise to a signal proportional to the jump in $f - f_e$ (Figure 2b). This is proportional to the shielding current i_s which gives rise to the molar susceptibility of the lamella $\chi = -\mu_0 L q^2 / 4 m_1 \Sigma_i r_i^2$; q is the charge of the electron pairs of mass m_1 moving in orbits of radius r_i; L and μ_0 are Avogadro number and the vacuum permeability. The radius of the orbits is obtained from the normal metal area $O = \Phi_0 / \triangle_0 H_z \approx 6.6\ \mu m^2$ when $\triangle_0 H_z$ is the periodicity near $H_z = 0$.[2] The energy for the ground state is $E_m = A(m-f)^2$ where $A(\mu K) = 694.5 (2 m_e / m_1) / O(\mu m^2)$, m_e is the free electron mass.[2] In the presence of JJ the cylindrical symmetry is destroyed and V mixes states of different quantum number m giving E/A **versus** f_e in Figure 2a.

The electrochemistry is based on work done to determine the thermodynamic properties of metal in ammonia solutions in,[3]

$Pt|Na|Na^+$ in β-alumina $|Na^+(am) \ldots e^-(am)|Pt|Na$ where $Na(s) = Na^+(am) + e^-(am)$

is the cell reaction, with $\triangle S^\circ(e^-(am)) = 154 \pm 20$ J/mole/K and $\triangle H^\circ(e^-(am)) = -95 \pm 10$ kJ/mole. In this work, the 1;2:3 ceramic replaces the Na(am) system and a $CuBr_2$-CH_3OH solution is equivalent to the β-alumina containing Na^+. In (1) $\triangle H$ is due to the the heat of formation of $Cu^{2+}(1{:}2{:}3)$; $\triangle S$ is due to the wntropy of formation of $e^-(1{:}2{:}3)$ because at 25 °C (CRC): $\triangle H_f(\frac{1}{2}Cu^{2+}(aq)) = 32.85$kJ and $\triangle S_f(\frac{1}{2}Cu^{2+}(aq)) = -65.13$J/K. Then in the absence of other reactions at electrochemical equilibrium the emf due to Galvani potentials **versus** T give:[2] $\triangle H_f(\frac{1}{2}Cu^{2+}(1{:}2{:}3)) + \triangle H_f(e^-(1{:}2{:}3)) = 29.7$ kJ±25% or, $\triangle H_f(e^-(1{:}2{:}3)) \approx 0$ and $\triangle S\ (\frac{1}{2}Cu^{2+}(1{:}2{:}3)) + \triangle S_f(e^-(1{:}2{:}3)) = 212$ J±15% or $\triangle S_f(e^-(1{:}2{:}3)) \approx 277$J/K/$e^-$. Thus thermodynamics gives the classical picture of the spin-glass to be very similar to the metal in ammonia solutions.

Power dissipation measurements,[4,5] of various superconductors at penetration depths of ≈5μm, have given insight into flux quantization in single crystals and ceramics. Very little is known about the ground state of the superconductor. At the rf frequencies used in the present work, the normal metal penetration depth is greater than the size of the lamellae dispersed in the epoxy matrix and, therefore the effect that a finite magnetic field has on the formation of a a mixed superconducting state may be investigated. Induction measurements have already been carried out in a direction parallel to the static and the rf fields at 7 kHz **versus** H_z = ± 20 Oe. by Jeffries **et al.**[5] The harmonic analysis by these authors indicates that the power dissipation is due to the spinglass behavior of the ceramic (Ebner and Stroud).[6]

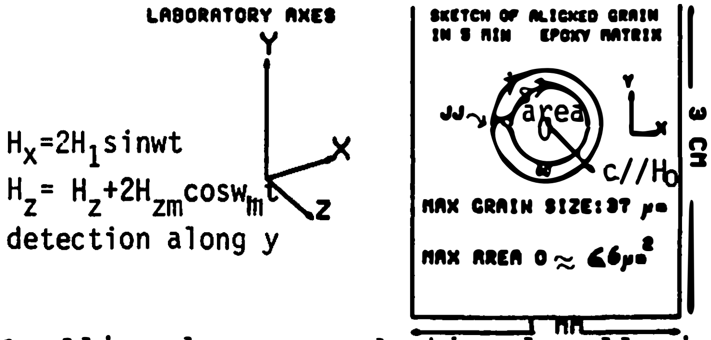

FIGURE 1 Aligned superconducting lamella in epoxy matrix.

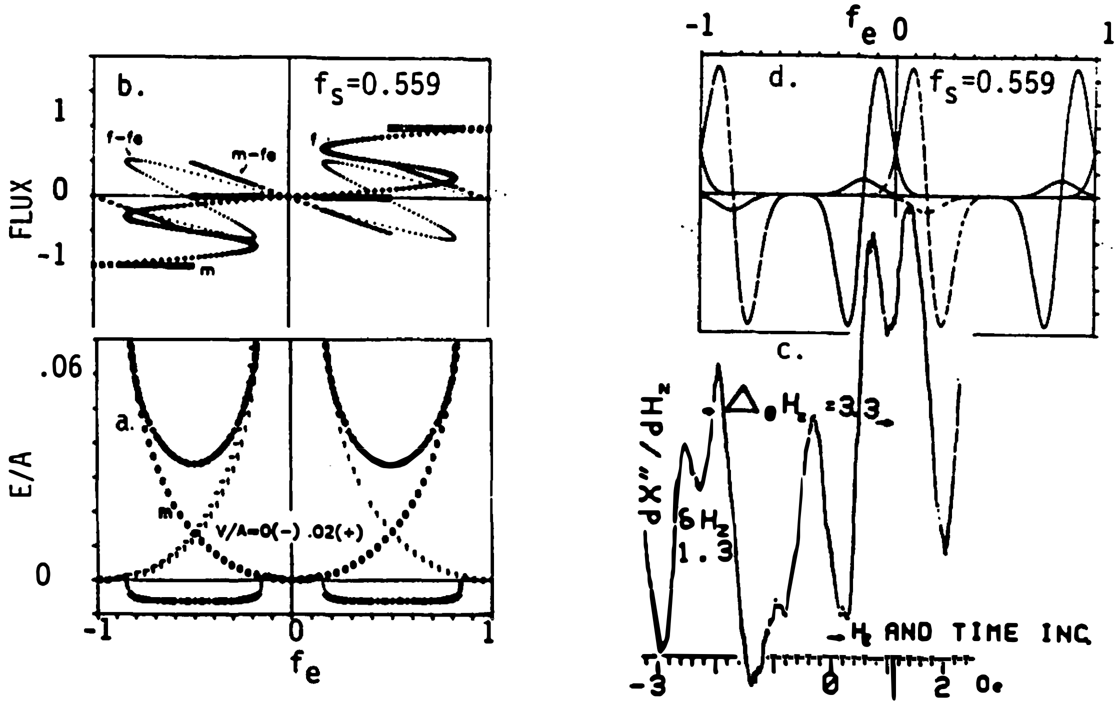

FIGURE 2 TYPICAL RF DISSIPATION SIGNAL AND INTERPRETATION.[2]

EXPERIMENTAL

The preparation of ceramics and single crystals and the measurements were done as described previously.[2] The samples were cooled to T_c at $H_z = 0\pm.05$ Oe and with the rf fields disconnected. Equilibrium was achieved by cycling the samples through T_c at least once before taking the measurement. The sample composition was determined by XRD, XRF and EPR absorption at room temperature. The susceptibility was calibrated using a free radical reference.[7] Figure 3a shows the dissipation signal **versus** time as T increases above T_c. The field is swept every 2.6s by ±10 Oe about $H_z = 0$. The amplitude in a common superconductor decays exponentially as $T \to T_c$ (Figure 3a). The signal in samples of different Tl composition decays near T_c showing oscillations in amplitude.

DISCUSSION AND CONCLUSIONS

We have characterized the high T_c superconductors in the normal state by the classical measure of disorder, the entropy of formation. The rf dissipation measurements describe the ground state for the superconducting lamellae. The diamagnetic susceptibility signal is due to the change in the shielding current when $df/df_e \to \infty$ in Figure 2b, giving for a single crystal the mass susceptibility $\chi = -3$ E-7. Then assuming the number of electron pairs in the ring is $\approx 10^{24}/m^3$, the value of χ can be used to estimate the thickness t of the superconducting ring; t= 40 nm when O determines the radius $r_i \approx 1.5\ \mu m$, **i.e.**,

$$\chi_d = -1.07*10^{13}/MW(Dalton)\ (2m_e/m_1)\ \Sigma_i r_i^2 = -3*10^{-7} \qquad (3)$$

where $MW = M_{uc}*O*h/(a*b*c)$ is the lamella weight when M_{uc} is the molecular weight of the unit cell (a,b,c) and the number of i pairs is given by $2\pi r_i t*h*10^{24}$. Also, as $T \to T_c$ the oscillations in amplitude may be due to currents between regions or grains of differing composition, in ceramics and in crystals.

ACKNOWLEDGEMENTS

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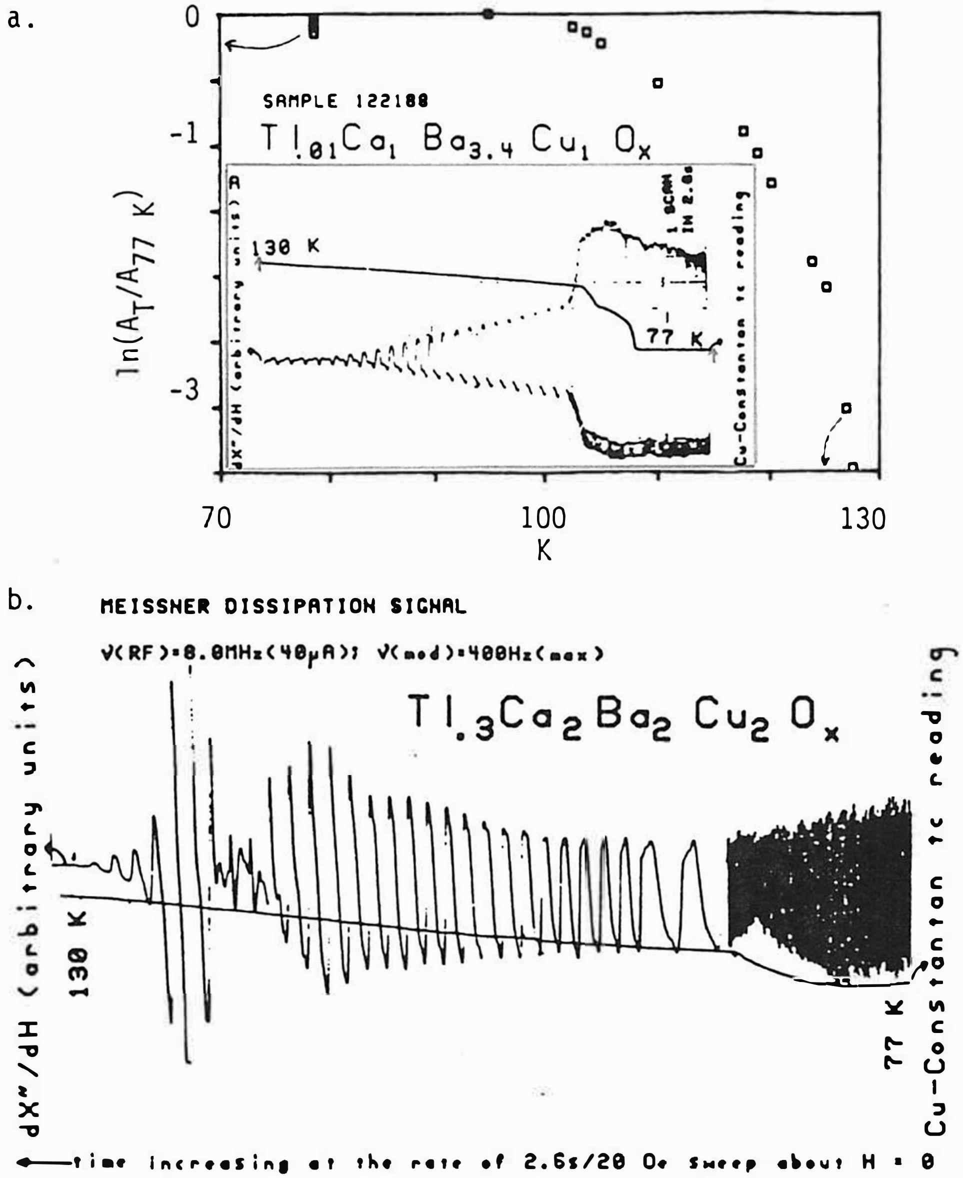

FIGURE 3 T_C determined from rf dissipation signal.

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