Chapter 3

Mercury based high temperature cuprate superconductors

Ülker Onbaşlı

Marmara University, Faculty of Science & Letts., Physics Department
(Retired Faculty & Senior Researcher)

III.1. Introduction

In 1990s, semiconductor technology reached to its limits at least by means of computer technology. In order to produce the fastest and the most compact computers, the semiconductor materials such as gallium arsenide, silicon were cut to obtain the minimum chip size. On the other hand, minimization process of semiconductors accompanied with a “quantum well” problem. As soon as the smallest sized semiconductor chip is obtained, the electrons of the semiconductors start to behave like any kind of electron without any identity in the quantum well. In other words, it was understood that the semiconducting materials lose their intrinsic properties for utilization on computers. When I recognized the “quantum well” problem in

In recent years, semiconducting quantum wells are successfully utilized as absorbers in saturable absorber mirrors and in electro absorption modulators. They are also used to make high electron mobility transistors which are used in low-noise electronics. Quantum well infrared photo-detectors are also based on quantum wells, and are utilized for infrared imaging.

Correspondence/Reprint request: Prof. Dr. Ülker Onbaşlı, Ridvanpaşa cad., 3.Sok., 85/12, Göztepe 34730 İstanbul, Turkey. E-mail: phonon@doruk.net.tr
experiences on some new materials for both scientific and technological semiconductors, I decided to search for new horizons to extend my view and purposes. After the discovery of high temperature cuprate superconductors it was a big challenge doing research in this new and promising area. From this viewpoint, my research adventure on superconductivity started when I was in Istanbul in 1990. Most of the experimental works on superconductivity have been carried out in the well equipped laboratories located in the United States and Europe. Hence, my first synthesis on mercury cuprate high temperature superconductors has been realized in Colorado University in 1993.

Magnetic measurements have been done at the National Institute of Standards and Technology (NIST). Thereafter, the experimental researches went on in Florida State University and High magnetic field laboratory in Florida. All of the magnetic measurements have been carried out by superconducting quantum interference device, SQUID.

Nevertheless, some magnetic susceptibility measurements have been realized by SQUID in Kammerling Onnes laboratory in Holland.

At beginning of the new Millennium I have achieved both of the preparation process and the resistivity versus temperature, Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD) measurement steps in Istanbul, Turkey.

Hence, chapter III is devoted to the investigation of the oxide layered high temperature superconductors by means brief review of relevant theories for superconductivity, their thermodynamics, magnetic and electrical properties, and some new approaches in calculation of critical current density without transport measurements, etc. Due to the volatile future of supercurrent, it is known that the measurement of “transport current” has high difficulties with inevitable ambiguity. By means of dealing with the currents of the order of $10^6$-$10^8$ Amper/cm² results in many experimental complications. So that the estimation of the order of magnitude of the supercurrent in advance, has a great importance in both science and technology. Moreover, the symmetry breakings in mercury based d-wave superconductors have been investigated as a new and charming topic for both theoreticians and experimentalists. Determination of paramagnetic Meissner effect temperature is crucial for some aspects so that a new method is introduced to extend comprehension about the formation of mass in high temperature d-wave superconductors by means of determination of electroweak symmetry breaking that results occurrence of Higgs bosons at Paramagnetic Meissner effect temperature. This will open-up a road and lead high energy physics and astrophysics researches, as well. Ultimately, the precise experimental calculation of the wave length of the topological
solitons, namely Segah solitons, in the d-wave superconductor corresponds to ultraviolet region that completes the missing part of high spin open string theory.

This chapter consists of two parts, as the first part is related to the general properties of the superconducting state, the second part represents some selected publications and international conference presentations on the mercury based copper oxide layered high temperature superconductors prepared.

### III.1.1. Milestones of superconductivity

I am glad having the chance to write down these sentences at the hundredth anniversary of the discovery of superconductivity.

As is known, superconductivity was discovered by Kamerlingh Onnes in 1911 [1]. First discovered superconducting material was metallic mercury element with the Meissner critical transition temperature, $T_c$ of 4.2 Kelvin. The most predominant feature of superconductivity is the exhibition of zero resistivity as shown in Figure 1 at which the mercury has no resistance below the $T_c$.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** The resistance versus temperature curve of the metallic mercury element. The superconducting transition occurs at 4.2K.

The most important fundamental property of the superconducting state is the Meissner effect, which was discovered by Meissner and Oshenfeld in 1933 [2].

The Meissner effect that corresponds to a diamagnetic response observed on the magnetic susceptibility data as shown for one of the superconductors (Figure 2).
Figure 2. Zero Field Cooled (ZFC) magnetic susceptibility ($\chi$) versus temperature curves for superconductors [3].

Figure 3. The repulsion of magnetic flux by a superconducting material when it is cooled under Meissner critical transition temperature.

Simply, the Meissner effect is the occurrence of the flux expulsion below $T_c$ that manifests itself as a diamagnetic response to the external magnetic field. The manifestation is displayed in Figure 3, a magnet is levitated by the superconductor due to the occurrence of Meissner effect.

In 1935, one of the theoretical explanations of the Meissner effect came out by London equations which were developed by F. London and H. London [4]. London brothers proposed two equations for electric and magnetic fields and they showed that magnetic field decays exponentially inside the superconductor in terms of a parameter called as the London penetration depth, $\lambda_L$ (Figure 4). The London penetration depth represents the length at which the magnetic field inside the superconductor decays to $H_0/2.7182$ where $H_0$ is applied magnetic field.

Very early explanations on the theory of superconductivity had started in 1940’s in Russia. Bogoliubov introduced coherent mixtures of particles and holes to describe superconductors and also derived collective excited states of quasi-particles. The condition for determining the transformation from ordinary fermionic electron to the bosonic quasi-particle representation was
 firstly developed by Bogoliubov. The Bogoliubov transformation is the fundamental essence for the BCS (Bardeen Cooper Schriefer) theory, was introduced almost ten years later in USA. The bosonic quasi-particle representation was named as Cooper pairs by Bardeen Cooper and Schriefer. Bogoliubov transformation method is equivalent to BCS theory of superconductivity, which is expressed in the following paragraph [5,6].

In 1950, Ginzburg & Landau developed a macroscopic theory of the superconductivity based on the second order phase transition theory and introduced one of the most important parameters i.e the order parameter, $\psi(\vec{r})$ varying with the position vector, $\vec{r}$, which describes the superconducting state with the phase difference, $\phi$ [7]. Individual electrons of the normal state, that obey Fermi-Dirac statistics, are transformed into bosonic Cooper pairs with zero spin during the superconducting transition. Hence, the superconducting system is described by a unique complex quantum wave function, $\psi(\vec{r})$.

$$\psi(\vec{r}) = |\psi(\vec{r})| e^{i\phi(\vec{r})}$$ (1)

Where, $|\psi(\vec{r})|$ and $\phi(\vec{r})$ are the amplitude of superconducting order parameter and phase function of position vector, respectively.

In 1957, Abrikosov introduced Type II superconductors and theoretically predicted the flux penetration and the vortex state in superconductors [8].

In 1967, the experimental verification of the vortex state has been determined in Lead-Indium alloy (Figure 5).

In Figure 6, the main difference between Type I and Type II superconductors has been schematically shown in the context of magnetization versus applied magnetic field curves. In Figure 6 (a), the superconductor

**Figure 4.** Schematic view of penetration of magnetic field into a superconductor.
Figure 5. The direct observation of individual flux lines in type II lead-indium alloy rod [9].

Figure 6. Magnetization versus applied magnetic field curves for (a) Type I (b) Type II superconductors.

totally expels the applied magnetic field and exhibits perfect diamagnetism up to the thermodynamical critical magnetic field of $H_c$. Above $H_c$, the system is in the non-superconducting state. The superconductor that exhibits perfect diamagnetic response that is classified as Type I superconductor.

In Type II superconductors, the system exhibits perfect diamagnetism up to the lower critical magnetic field of $H_{c1}$. If one goes on to increase the applied magnetic field, the magnetic field begins to penetrate through the superconductor. This means that the system contains normal and
superconducting regions at the same time but the system still is a superconductor. But above the upper critical filed of $H_{c2}$, the system is in the non-superconducting state. The superconductor that exhibits this type of magnetic property is called as Type II superconductor (Figure 6 (b)).

In 1957, Bardeen, Cooper and Schrieffer proposed a microscopic BCS theory of Type I superconductors [10]. BCS theory is based on the formation of slightly attractive electron-electron interaction via quantized lattice vibrations, namely phonons that results the emanation of Cooper pairs close to the Fermi level at low temperatures. Cooper pair consists of two electrons having opposite spin and momentum that are bound together at low temperatures via harmonized phonons. BCS theory also indicates an energy gap between free electron energy states and Cooper pair energy states. Principle mechanism is also valid for the ab-plane of layered structure high temperature superconductors, as well. The three dimensional superconductivity mechanism in cuprate superconductors will be interpreted in the Chapter IV.

Despite of the fact that up till now various theoretical models have already been proposed for explaining the mechanism of superconductivity, the mechanism has not totally understood yet. Some of the remarkable theories that explain magnetic properties of the superconductor are Bean critical state model, Kim-Anderson model, Taff model etc.

According to Lehendorf, a fundamental treatment of the dynamics of vortices in hard superconductors was proposed by Bean critical state model and Kim&Anderson model which are still valid [11].

Bean critical state model explains various magnetic properties for hard superconductors as well as high temperature superconductors [11]. Bean critical state model is safely used under lower critical magnetic field value, $H_{c1}$. The most crucial achievement of the Bean critical state model is to calculate critical current density, $J_c$, via magnetization difference between increasing and decreasing magnetization branches, $\Delta M$, on $M-H$ hysteresis curves [12,13]. As an example, we have arranged magnetic hysteresis measurements on the mercury cuprate superconductors prepared. In Figure 7, the $\Delta M$ quantity at the vicinity of lower critical magnetic field has been shown for one of the mercury cuprate samples synthesized.

Some limitations of the Bean critical state model that do not completely reflect the reality of the superconducting state such as the critical current is independent of the applied magnetic fields were resolved by thermally activated flux creep theory which was proposed by Anderson and Kim [11].

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1Ideally, hard superconductors represent a Type II superconductor with an infinite pinning force (or critical current density). Moreover, Type II superconductors are mechanically harder than Type I superconductors. The term “hard” also emphasizes both Meissner critical transition temperature and critical magnetic fields.
Figure 7. Magnetization versus applied magnetic field hysteresis curve of the mercury cuprate high temperature superconductor at 25K. At the lower critical magnetic field of, $H_{c1}$, the magnetization difference $\Delta M$ is shown [14].

Figure 8. Voltage versus current curve of Type II superconductors. The illustration also shows how to define critical current, $I_c$ via transport measurement [15].

In current transport measurements of Type II superconductors, three main parts with different behaviors are marked as shown in Figure 8. At low current region, $I-V$ curve is linear and this region is called as TAFF (Thermally Assisted Flux Flow) region. As the current increases to intermediate level, the system begins to exhibit nonlinear $I-V$ characteristics in flux creep regime. For high currents, the $I-V$ curve is again linear that corresponds to flux flow region [15].
The flux creep phenomenon was explained by Kim-Anderson model which is based on thermally activated flux hoping between pinning points [16, 17]. Kim-Anderson theory also proposed “flux bundles”. The flux bundles represent the cluster of neighboring fluxoids, coupled by their mutual interactions, which is supposed to behave collectively in each thermally activated event [18].

An edge breaking discovery occurred in 1962 by Brian Josephson who discovered the Josephson effect at which the electron pairs quantum mechanically tunnel the thin insulating layer due to the phase difference between superconducting layers [19]. The structure, at which two superconductors separated by a thin insulating layer, is known as Josephson junction (Figure 9). The Cooper pairs on each side of the junction are represented by a quantum wave function. The supercurrent flow in the Josephson junction is determined by the gradient of phase difference (Eq. 2).

\[
\phi = \sin \frac{\Delta \phi}{\sin \phi}
\]

where \(I_s\), \(I_c\) and \(\Delta \phi\) represent the super-current, maximum critical current and phase difference, respectively.

In the AC Josephson effect, a Josephson junction emits an electromagnetic wave with a characteristic angular frequency, \(\omega\) which is proportional to the voltage applied across the junction.
$$\frac{d}{dt}(\Delta \phi) = \frac{2eV}{\hbar} = \omega$$

(3)

where $V$ is the voltage applied and $\hbar$ is Heisenberg constant. ($\hbar=h/2\pi$ where $h$ is Planck constant)

Discovery of Josephson effect not only opened a huge door to the various technological applications with superconductors such as Superconducting Quantum Interference Device (SQUID), qubit (quantum bit) operations etc. but also gave an insight for explaining the conductivity mechanism in layered cuprate superconductors. In this context, P.W. Anderson’s Interlayer theory, which is based on electromagnetic coupling between superconducting layers via Josephson effect, enlightens our scientific comprehension about the electrical conductivity mechanism in copper oxide layered superconductors. The details of the theory will be discussed in Chapter IV.

### III.1.2. Thermodynamics of the superconducting state

The onset of superconductivity manifests itself as the occurrence of some sharp changes in various physical parameters of the system. As is seen from Figure 10, both resistivity and heat capacity of the material change suddenly at the critical transition temperature, $T_c$ due to superconducting transition process.

**Figure 10.** Illustrations of two basic characteristics of a superconductor. (a) Resistivity versus temperature curves for superconducting and non-superconducting materials. (b) The typical specific heat versus temperature curve of low temperature superconductors.
Since superconducting transition is a second order phase transition, it is possible to examine the phase diagram of superconductors in exactly the same manner as one would consider the thermodynamics of a liquid-gas phase transition process [21]. In this situation, the thermodynamic variables of pressure, $p$ and volume, $V$ are replaced by applied magnetic field, $H$ and magnetization, $M$.

According to the second law of thermodynamics,

$$dU = TdS - pdV$$  \hspace{1cm} (4)

where $U$ is the total internal energy, $T$ is the temperature and $S$ represents entropy. Eq. (4) is adapted to superconductors under the view of this analogy that is given in Eq. (5).

$$dU = TdS + HdM$$  \hspace{1cm} (5)

Since the temperature, $T$ and applied magnetic field, $H$ are independent variables, it is convenient to choose Gibbs free energy for defining the transition from normal to superconducting state. Gibbs free energy, $G$ is defined as

$$G(T, H) = U - TS - HM$$  \hspace{1cm} (6)

When the temperature is constant, the differential of the expression yields to Eq. (7).

$$dG(T,H) = - MdH$$  \hspace{1cm} (7)

In non-superconducting state (i.e. normal state), Gibbs free energy for the superconductor is given as

$$G_N(T,H) = G_N(T,0)$$  \hspace{1cm} (8)

According to Meissner effect, the magnetic field inside the superconductor is zero so that

$$H_{inside} = H + 4\pi M = 0$$

$$H = -4\pi M$$  \hspace{1cm} (9)
At a constant temperature, Eq. (7) is rewritten by using Eq. (9) and integrating as

\[ \int_{G_S(T,0)}^{G_S(T,H)} dG_s = \int_0^H -\frac{H}{4\pi} dH \]

\[ G_S(T,H) - G_s(T,0) = \frac{H^2}{8\pi} \]  

(10)

Eq. (10) represents the energy released (gained) due to Meissner effect. If the applied magnetic field is taken as thermodynamical critical magnetic field of \( H_c \),

\[ G_N(T,H_c) = G_N(T,0) \]

\[ G_S(T,H_c) = G_S(T,0) + \frac{H_c^2}{8\pi} \]  

(11)

Moreover, two phases are in thermodynamic equilibrium at critical magnetic field.

\[ G_N(T,H_c) = G_S(T,H_c) \]

So that one can find the relation between normal and superconducting Gibbs free energies as given in Eq. (12). This situation is illustrated in Figure 11.

\[ G_N(T,0) = G_S(T,0) + \frac{H_c^2}{8\pi} \]  

(12)

\[ \text{Figure 11. Applied magnetic field dependence to Gibbs free energy.} \]
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The quantity $H_c^2/8\pi$ is called as superconducting condensation energy which is a measure of free energy gained per unit volume in the superconducting state compared with the non-superconducting phase at the same temperature [21].

The entropy of the system during the superconducting transition is calculated by very well known expression,

$$S = -\left(\frac{dG}{dT}\right)$$  \hspace{1cm} (13)

The entropy difference, $\Delta S$ is given in Eq. (14).

$$\Delta S = S_S - S_N = \frac{H_c}{4\pi} \left(\frac{dH_c}{dT}\right)$$ \hspace{1cm} (14)

According to Eq. (14), it is concluded that the entropy of the normal state is greater than that of superconducting state. So that the order of the superconducting state is considered to be higher than that of the normal state.

### III.1.3. Discovery of high temperature superconductors

The discovery of La-Sr-Cu-O family superconductors in 1986 has a special place in the history of superconductivity. Müller and Bednorz, created the brittle ceramic compound (La-Sr-Cu-O family superconductors) that conducted with zero resistance at the highest temperature known up till that time: $T_c=40$ K [22]. What made this discovery so remarkable was that the ceramics are normally insulators and not conduct electricity. Due to this fact researchers had not considered them as possible high-temperature superconductor candidates.

Soon after this discovery of La-Sr-Cu-O family superconductors, a large number of mixed copper oxides namely cuprates are found to be superconductors such as yttrium barium copper oxide, Y-Ba-Cu-O; bismuth strontium calcium copper oxide, Bi-Sr-Ca-Cu-O; mercury barium calcium copper oxide, Hg-Ba-Ca-Cu-O.

In Figure 12, the time evolution of some low and high temperature superconductors can be seen.

It is remarkable that the Hg-based cuprate superconductors exhibit the highest superconducting Meissner transition temperature of 140K [23] at
normal atmospheric pressure among the other high temperature superconducting materials (Figure 12). Moreover, it is possible to increase the critical transition temperature by applying pressure in the order of giga Pascal.

**III.1.4. Mercury cuprate superconductors**

In this section a brief history of the mercury based copper oxide layered high temperature superconductors is represented.

The first mercury based high temperature superconductor was HgBa$_2$CuO$_{4+x}$ (Hg–1201) material with Meissner transition at $T_c$=98K, which
was synthesized by Putilin et al. in 1993 [25]. In the same year, Schilling et al. reached the critical transition temperature to 134K for the mixture of HgBa\(_2\)CaCu\(_2\)O\(_{7+x}\) (Hg–1212) and HgBa\(_2\)Ca\(_2\)Cu\(_3\)O\(_{8+x}\) (Hg–1223) materials at the normal atmospheric pressure [26]. Subsequently, Gao et al., made an achievement by increasing the critical transition temperature to 153K by applying 150 \times 10^8 Pa pressure to the HgBa\(_2\)Ca\(_2\)Cu\(_3\)O\(_{8+x}\) superconductor [27]. Ihara et al. also attained the \(T_c=156K\) by the application of 250.10\(^8\) Pa pressure to the superconducting material contains both Hg–1223 and Hg–1234 phases [28]. Afterwards, in 1996, Onbaşlı et al. acquired the highest critical transition temperature of 138K at normal atmospheric pressure in the optimally oxygen doped mercury cuprates which contains Hg-1212 /Hg-1223 mixed phases [29]. Recently, the new world record of \(T_c\) at the normal atmospheric pressure has been extended to 140K for the optimally oxygen doped mercury cuprate superconductor by Onbaşlı et al. [23].

References


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III.2. Selected publications related to mercury cuprate family superconductors

III.2.1. Transport properties of high-Tc mercury cuprates

U. ONBASLI et al.: Transport Properties of High-T, Mercury Cuprates 371
phys. stat. sol. (b) 194, 371 (1996)

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Department of Physics, University of Colorado, Boulder

U. Onbaşlı, T. Wang, Naziripour R. Tellow, Kiehl and A. M. Hermann

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Abstract

Measurements of dc and ac susceptibility, resistivity, Hall effect, and thermoelectric power (TEP) on pure phase Hg-1223 and mixed phase Hg-1212-1223 cuprates are reported. The mixed phase compounds show the highest critical temperature (magnetic susceptibility onset of 140 K). Both Hall effect and TEP data support an under doped state with hole-like conduction. Oxygen annealing reduces the Hall coefficient (increasing the concentration of holes) and lowers the TEP (increasing the Fermi energy) features which can be explained by a simple Fermi-gas picture. The Hall coefficient which increases linearly with temperature and the negative temperature coefficient of the TEP, however, cannot be explained by single-hand Fermi-gas or -liquid theory, unless one introduces energy dependent carrier scattering. Estimates of the highest critical temperature based on the universality observed in the thermopower data for the cuprates suggest that 140 K is near the maximum one might expect for the Hg cuprates under optimal doping at atmospheric pressure.

Dedicated to Professor Dr. K. W. BOER on the occasion of his 70th birthday
III.2.2. Magnetic measurement of critical currents on mercury cuprates

Ülker Onbaşlı¹, Semra Öztürk¹ and Yusuf S. Hasçiçek²
¹University of Marmara, Fen-Ed.Fak. Ziverbey 81040, Istanbul-Turkey
²National High Magnetic Field Laboratory, Tallahassee, FL, U.S.A

Abstract

Mercury based superconducting oxides were fabricated by a unique melt textured process, called QMG (quenched melt growth) procedure. The QMG bulk superconductors with zero resistance of 136 K, from magnetic measurements are expected to realize new applications, such as current leads, bearings and bulk magnets because of its high critical current density $J_c$, strong links between the grains, and size respectively. Analysis of critical currents, deduced from dynamic hysteresis loops, was made in the frame of the Bean Critical State model. The QMG bulk superconductors of Hg-1223, have very high critical current densities, $J_c=3.75 \times 10^7$ A/cm$^2$ at 4.2 K and 1 T, $J_c=6.53 \times 10^7$ A/cm$^2$ at 4.2 K and 0.25 T, $J_c=1.25 \times 10^6$ A/cm$^2$ at 77 K and 0.25 T. The grain size of the samples have been determined by random intercept method from SEM (scanning electron microscope) measurements. Moreover, it was determined that the superconducting bulk materials are thermally stable above 100 K.

I. Introduction

Oxide superconductors are very attractive not only for their high critical temperatures $T_c$, but also for having very high critical current densities $J_c$ and irreversibility lines. Moreover, after the discovery of a new family of superconducting materials, the mercury based copper oxides, [1,2] has developed further interest in high temperature superconductors (HTS). A particularly pronounced feature of the mercury-based copper oxides is that they have the highest Meissner transition temperatures of 138 K at ambient pressure [3] and
Figure 1. A QMG-mercury cuprate single grain with a perfect layered structure. SEM was taken at 5.0 T, 20 kV, ESD X5350.

164 K, under quasihydrostatic pressure [4]. Both were achieved for HgBa$_2$Ca$_2$Cu$_3$O$_{8+y}$ (Hg-1223) polycrystalline mercury cuprates which were synthesized by the solid state reaction technique (SSRT).

In this work, we report the critical current density $J_c$ values of a unique quenched melt growth (QMG) [5] mercury based superconducting oxide, Hg-1223 samples with $T_c=136$ K for the first time. We determined the critical current densities, deduced from dynamic hysteresis loops, at 4.2 K, and 77 K, which were calculated in the frame of the Bean Critical State model [6]. The grain size of the Hg-1223 samples was found from SEM measurements. By using the random intercept method the grain size was determined to be 1.5 μm (Figure 1).

The QMG method, used for preparation of mercury cuprate bulk material, improves $J_c$ and enables us to control the irreversibility line and move it to higher temperatures, by some additional treatment of the material. Using melt textured growth (MTG) process for YBaCuO, the weak link problem was first solved by Jin et al [7]. By introducing the pinning centers into bulk YBaCuO, $J_c$ values have been improved and have reached $10^4$-$10^5$ A/cm$^2$ at 77 K in magnetic fields of several Tesla [8-10].

Nevertheless, providing additional pinning sites to oxide superconductors made controlling of the phase diagram of the system very difficult as well as the usage of the material for particular applications. In this work, we report
the study of the unique feature observed on QMG Hg-1223 samples, the effect of strong surface pinning at low temperatures over a wide range of magnetic fields up to 5 T (Figure 2). Furthermore, the process of QMG provided some intrinsic bulk pinning centers, without surface barrier pinning at high temperatures (Figure 3).
When dealing with melt process superconductors such as YBaCuO [11], it was experimentally determined that the magnetization of the samples was found to be independent of the sample thickness indicating that shielding currents are localized within the individual grains. An identical effect has been observed by us on the Hg-1223 samples and we have assumed that the state of current loop is represented by the average size (t) of the grains.

II. Experimental

The mercury cuprate bulk samples, Hg-1223 have been prepared by the quenched melt growth method by using the four nine purity materials of BaO, CaO, CuO and HgO. Both dc magnetic susceptibility and the dynamic hysteresis measurements were performed by the Quantum Design SQUID Susceptometer, model MPMS-5S. According to dc magnetic susceptibility measurements, it was determined that the Meissner on set temperature was the same, $T_c = 136K$ for the Hg-1223 samples which were kept in different conditions. Some from the same batch were kept in air and in argon before being measured for several months, the other batch was measured as prepared. Furthermore, no degradation was observed, because of the fact that the Hg-1223 samples were mechanically very hard, dense and stiff.

For the dc susceptibility measurements the magnetic field of $10^{-3}$ T was applied to the samples. The same swept rate of 0.025 T/s was used for the hysteresis measurements performed at various temperatures.

With respect to the Bean Critical State approach, the $J_c$ values which have been deduced from Figure 2 and calculated by Equation (3). Referring to the SEM picture using random intercept method, the average grain size $t$ in (3) was determined as 1.5 μm.

The critical current densities $J_c$, were calculated with respect to the Bean Critical State model that relates magnetic moment (m) to critical current density ($J_c$) for superconducting samples which are large enough when compared with the penetration depth ($\lambda$). For the applied magnetic field $H$ parallel to c-axis $H//C$, the critical current $J_y$ flows in the a-b plane of the sample.

Hence we write,

$$\nabla \times H = J$$  \hspace{1cm} (1)
\[-\frac{\partial H_z}{\partial x} = J_y\] (2)

In the critical state $J_c$ is written as

$$J_c = 30 \frac{4\pi \Delta M}{t}$$ (3)

Where, $\Delta M$ is the difference in magnetization between the increasing and the decreasing field branches, and $t$ is the average grain size. From Figure 1, the average grain size of the Hg-1223 sample is $t=1.5\,\mu m$. From hysteresis measurements we determined the critical current densities of QMG mercury cuprate samples that flows in the a-b plane, $J_c =6.53 \times 10^7 \, A/cm^2$ at 4.2 K and 0.25 T (Fig. 2). The same calculation was made at 77 K and 0.25 T, resulting $J_c =1.25 \times 10^6 A/cm^2$ (Fig. 3). For the higher fields up to 1 Tesla, the critical current density of the sample was found to be $3.75 \times 10^7 \, A/cm^2$ at 4.2 K.

### III. Results

We first determined the fact that the unique QMG technique provided us with non degrading very dense, rigid superconducting mercury cuprate material with a very high transition temperature of 136K. Furthermore, both the melt technique and appropriate oxygen annealing were found to be very important in stabilizing the Hg-cuprate samples prepared at atmospheric pressure. This result has been confirmed by dc-SQUID measurements performed on Hg-1223 samples which have been kept in air for several months after being synthesized, (Figure 4).

Referring to Figure 2, the hysteresis measurements made at 4.2K which displays very asymmetric hysteresis loops with respect to increasing versus decreasing field branches, where both a strong surface effect and bulk pinning occur. Figure 3 displays the symmetric hysteresis loops with respect to increasing versus decreasing field branches where a weak surface effect occurs and bulk pinning dominates. By combining the result obtained from Figure 2 and Figure 3, it is seen that as the temperature increases so the weak-link between the grains decreases. This behavior can be easily
understood by recalling the thermally assisted flux flow model (TAFF) in HTS oxides.

Hence, at higher temperatures $T \geq 77\,\text{K}$, the surface pinning vanishes whereas bulk pinning dominates for QMG mercury cuprates. One further point is possible unpaired $\text{Cu}^{+2}$ ions give rise to the paramagnetic tendency of the samples at high applied field values. From Figure 2 and Figure 3, it is seen that this behavior starts beyond $3\,\text{T}$ at $4.2\,\text{K}$ and that $1.5\,\text{T}$ at $77\,\text{K}$ for the QMG mercury cuprates.

For the Hg-1223 samples prepared, the pinning mechanism for the flux lines was favorably attributed to the presence of the pins such as CuO-planes, some dislocations and the large atomic cell [3]. Moreover, the QMG technique also provides some possible unpaired $\text{Cu}^{+2}$ ions that act as intrinsic paramagnetic sites resulting in samples which do not exhibit any upper critical field $\mathcal{H}_c^2$.

This behavior allows the QMG mercury cuprates to be safely used for particular applications in high fields and at the temperatures $T > 120\,\text{K}$. Noting Figure 3 where a weak surface effect occurs and bulk pinning dominates, the bulk pinning results in a paramagnetic behavior at fields of

**Figure 4.** The magnetic moment, $m$ versus temperature at $10^{-3}\,\text{T}$. The Meissner transition temperature, $T_c=136\,\text{K}$. 

about 1.5 T. No upper critical field value is defined. The lower critical field \( H_{c1} = 0.25 \) T, remained unchanged with temperature.

According to Figure 3, with its feature of displaying low anisotropy at high temperatures e.g. \( T = 77K \), at considerably low field \( H \leq 0.25T \), the QMG mercury cuprates will be a suitable candidate for the applications in the areas where liquid oxygen has a specialized function.

In high \( T_c \) superconductors, a line called irreversibility \( H_{irr} \) exists and lies between \( H_{c1} \) and \( H_{c2} \) of lower and upper critical fields, corresponding to the Meissner State and the normal states of the superconducting materials respectively. Above this line the fluxoids form no lattice and move freely, such a state is called the vortex glass. In most experimental work the irreversibility line is determined by a mobility criterion for the vortex lattice (VL) [12]. The origin of the irreversibility line may be a first order melting transition of the vortex lattice, a transition from a vortex glass to a liquid, or a thermally driven depinning. As was suggested, these phenomena are intimately related [13].

From this theoretical point of view, for the QMG mercury cuprates referring to the dynamic hysteresis measurements there is neither \( H_{c2} \) nor \( H_{irr} \) can be described. As a consequence, no transition from a vortex glass to a liquid or thermal depinning is favored.

Noting Figure 5 the critical current density of the Hg-1223 sample at 4.2K decreases with applied magnetic field in accord with the exponential

![Figure 5](image)

**Figure 5.** The critical current density versus applied field at 4.2 K. The data were deduced from hysteresis measurements from Figure 2.
equation in the given inset of Fig. 5. The decay of $J_c$ due to flux creep was first described by [14].

**IV. Discussion**

For the multi-layered mercury cuprates with very high transition temperature at atmospheric pressure was attributed to the resonant coupling between the layers of the supercell structured Hg-1223 compound [3]. Referring to [15,16] the reason for the high $T_c$ values that exists in one layered mercury cuprate, HgCaCuO$_4$ (Hg-1201) samples was theoretically explained by electromagnetic coupling along the c-axis with the condensation energy of the superconductor.

We first addressed the fact that to improve $J_c$ without having any grain boundary weak-link problem at high temperature $T > 77K$, the QMG process can be successfully used for the Hg-1223 bulk superconductors. The method also provides some possible unpaired Cu$^{+2}$ ions that act as paramagnetic sites resulting in samples which do not exhibit any upper critical field $Hc_2$.

The paramagnetic behaviour of the hysteresis curves and weak surface pinning have been previously observed by Mota [17] in Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ single crystals at low temperatures and by Murakami [18] for melt processed rare earth-Ba-Cu-O samples at 77K. Furthermore, because of the fact the content of the unpaired Cu$^{+2}$ ions may be controlled, this gives rise to the upper critical field $Hc_2$ and that of the irreversibility line which in turn leads QMG Hg-cuprates being used for high temperature, high field applications.

For the Hg-1223 samples investigated, the high current density of $6.53 \times 10^7$ A/cm$^2$ makes it suitable for the current lead applications at liquid Helium temperature. The final and best suggestion is that with its feature of displaying low anisotropy at high temperatures, the QMG mercury cuprates will be a first-rate choice in the area of applications where liquid oxygen has a particular function.

**Acknowledgment**

We wish to thank the related members of NHMFL in Tallahassee and the department of Chemistry at University of Marmara-Istanbul. We would like to thank P.H. Kes and V.Kresin for many helpful discussions. We would also
like to thank Eric Lochner for his efforts on magnetic measurements performed at FSU.

References

5. Ü. Onbasli, unpublished.
III.2.3. Effect of oxygen post-annealing at the critical parameters of mercury cuprates

Ülker Onbaşlı
1University of Marmara, Fen-Ed.Fak. Ziverbey 81040, Istanbul-Turkey

Abstract

After being prepared by quenched melt growth technique (QMG), the mercury-1223 superconductors were annealed with oxygen for several times. According to the DC SQUID measurements performed at 10G, it was determined that the Meissner onset temperature, $T_c$, decreased by 10K (from 136 to 126K). The critical current densities, $J_c$, have been deduced from hysteresis loops, and were calculated by using the Bean Critical State model, at three different temperatures: $J_c \approx 2 \times 10^7$ A/cm$^2$ at 5K and 0.25T, which is about three times less than the value obtained without post-oxygen annealing; $J_c \approx 5.8 \times 10^4$ A/cm$^2$ at 77K and 0.02T, which is two orders of magnitude smaller than it used to be; $J_c \approx 3.6 \times 10^4$ A/cm$^2$ at 90K and 0.02T. Moreover, it was determined that the superconducting materials are thermally stable above 90K. The decrease in the critical parameters has been attributed to the formation of some mesoscopic defects that must be enhanced by further oxygen annealing.

I. Introduction

Mercury based superconductors have the potential to be used in various applications at 77K, due to their high $T_c$, high critical current density and, irreversibility lines.

To produce high quality Hg-1223 superconducting materials with good transport properties, control of the grain size and the Hg partial pressure are essential. We used the two-step quenched melt growth (QMG) procedure that enables us to control these properties. The two-step QMG technique was first reported by Onbaşlı et al. [1] for Hg-based superconductors. Various workers have investigated the effect of heat treatment in oxygen on the critical
parameters of mercury based superconductors [2-4]. Hofer et al. [2] investigated the oxygen doping dependence of effective mass anisotropy of \( HgBa_2CuO_x \), which increases as the oxygen content reduces. The effect of oxygen annealing temperature on the superconductivity of \( HgBa_2Ca_2Cu_3O_x \) thin films was determined by Kang et al. [3]. It was reported that optimally oxygen annealed thin films display the highest transition temperature of 133K, and \( J_c \approx 10^5 \) A/cm\(^2\) at 120K in zero field.

Fujinami et al. [4] determined the effect of over doping on the critical parameters of the \( HgBa_2Ca_2Cu_3O_x \) superconductors with \( T_c=133K \), prepared by high pressure synthesis. The magnetization experiments revealed that both the \( J_c \) and the irreversibility field, \( H_{irr} \), properties were improved as the oxygen doping (increase in holes) became heavier. It was previously determined by Onbaşlı et al. [5] that optimal doping with oxygen increases the concentration of holes, which results in an increase on the critical temperature, \( T_c=138K \), of mercury cuprate polycrystalline superconductors at normal atmospheric pressure.

In this work, the role of oxygen doping rate at the over doped state on the critical parameters of the quenched melt Hg-1223 samples has been investigated.

At the over doped state, oxygen doping decreases the electronic anisotropy of mercury cuprates, which results in the decrease of \( T_c, J_c \) and the critical field values.

2. Experimental

QMG Hg-1223 samples prepared by the QMG method were used for the measurements. The detailed information is given elsewhere [1]. After being synthesized, the samples were subjected to oxygen annealing twice at 300 and 200\(^0\)C for 12h. Both DC magnetic susceptibility vs. temperature and dynamic hysteresis measurements were performed by Quantum Design SQUID Susceptometer, model MPMS-5S. According to the SQUID data taken at 10G, the Meissner on set temperatures were obtained for optimally deposed QMGs, \( T_c=136K \) (Fig.1) and \( T_c=126K \) for the over doped samples (Fig. 2) from the same batch. For the hysteresis measurement performed at 5K, a sweep rate of 0.025T/s was used. Using Bean Critical State Model, \( J_c \) values have been deduced from Figs. 3 and 4 for 5and 90K, at the magnetic field, \( H \) applied parallel to the c-axis, \( H//c \). The critical currents \( J_y \) that flow in the ab-plane of the sample were calculated by Eq. (1).
In the critical state, $J_c$ is written as

$$J_c = 30 \frac{4\pi \Delta M}{t}$$  \hspace{1cm} (1)

**Figure 1.** The magnetic moment $m$ vs. temperature is at 10G. The Meissner transition temperature $T_c = 136$K for the optimally doped Hg-1223 (QMG).

**Figure 2.** Magnetization $M$ vs. temperature at 10G. Inset shows the transition temperature $T_c = 126$K for the over doped Hg-1223 (QMG).
Figure 3. Magnetization $M$ vs. applied field $H$ at 5K. An asymmetric hysteresis loop where surface pinning occurs.

Figure 4. Magnetization $M$ vs. applied field $H$ at 90K. An asymmetric hysteresis loop is displayed.
where \( t \) is the average grain size of the Hg-1223 samples and \( \Delta M \) is difference in magnetization between increasing and decreasing branches. The average grain size was determined from scanning electron microscope, SEM, measurements [1].

We have determined the \( J_c \) values of post-annealed mercury cuprate samples, \( J_c=2\times10^7 \text{ A/cm}^2 \) at 5K and 0.25T, \( J_c=5.8\times10^4 \text{ A/cm}^2 \) at 77K and 0.02T. It was also determined that the superconducting materials are thermally stable above 90K. Moreover, the critical current density was calculated to be \( J_c=3.6\times10^4 \text{ A/cm}^2 \) at 90K and 0.02T.

3. Results and discussion

The two-step QMG procedure provides control of the Hg partial pressure, which is essential to reduce the formation of undesirable phases, such as Hg-Ca-O and Hg-Ba-O, at the surface of superconducting growing material. It was found that annealing at 300°C for 12h in flowing oxygen provides an optimum doping for Hg-1223 (QMG) samples. The subsequent heat treatment, such as annealing at 200°C in oxygen pressure of 150 bar for several hours, results in the decrease of the critical parameters.

With respect to the transport measurements, we have determined that the Hg-1223 superconductors prepared by solid state reaction technique, display hole-like conduction. Moreover, optimum oxygen doping introduces more holes into the Hg-1223 phase responsible for superconductivity, which enabled us to achieve the highest value of \( T_c \) observed for Hg family at normal atmospheric pressure [5].

We could conclude that \( T_c \) increases with increasing hole doping level in the under doped region. Optimal oxygen annealing may result in oxygen ordering which is influential to superconductivity.

We note that the reduction in Meissner temperature and broadening of the transition width from normal to superconducting state, as seen from Figs. 1 and 2, may be attributed to the decoupling of superconducting layers.

At low temperatures such as 4.2K and 5 K, oxygen post-annealing does not change the order of magnitude of the \( J_c \) values at the applied field 0.25T.

The effect of post-annealing that is found to be more pronounced at higher temperatures, it lowers the magnitude of both \( J_c \), the critical fields \( B_{c1} \) and \( B_{c2} \). The related results are seen in Table 1 and Table 2.
Table 1. Post-oxygen annealed Hg-1223 (QMG); $T_c=126$K.

<table>
<thead>
<tr>
<th>$T$(K)</th>
<th>$J_c$ (A/cm$^2$)</th>
<th>$B_{c2}$ (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>$1.18\times10^7$</td>
<td>0.490</td>
</tr>
<tr>
<td>77</td>
<td>$1.65\times10^4$</td>
<td>0.070</td>
</tr>
<tr>
<td>90</td>
<td>$3.16\times10^4$</td>
<td>0.024</td>
</tr>
</tbody>
</table>

Table 2. Optimally oxygen annealed Hg-1223 (QMG); $T_c=136$K.

<table>
<thead>
<tr>
<th>$T$(K)</th>
<th>$J_c$ (A/cm$^2$) at $B_{c1}$</th>
<th>$B_{c1}$ (T)</th>
<th>$B_{c2}$ (T)</th>
<th>$J_c$ (A/cm$^2$) at $B_{c2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>$10^8$</td>
<td>0.35</td>
<td>3</td>
<td>$1.26\times10^7$</td>
</tr>
<tr>
<td>77</td>
<td>$10^6$</td>
<td>0.25</td>
<td>1.5</td>
<td>----</td>
</tr>
</tbody>
</table>

Figure 5. The $J_c$-$B_{c2}$-$T_c$ diagram of post-annealed Hg-1223 (QMG); $T_c=126$K.
Figure 5 displays the effect of temperature on $J_c$-$B_{c2}$-$T_c$ diagram of the over doped samples. Due to sudden dissipative rearrangement of magnetic flux within the superconductors, as the temperature rises from 5 to 90K, $J_c$ falls.

The irreversibility line (IL), which separates the vortex liquid in the field temperature ($H$-$T$) phase diagram, is an important problem in HTSC materials from the point of view of applications. Referring to dynamical hysteresis data of mercury cuprates prepared which do not display any transition from vortex solid to vortex liquid, because of the paramagnetic tendency of the material.

In conclusion, the anisotropy of magnetization was lowered by post-annealing of Hg-1223 (QMG) superconducting materials.

It was speculated that further oxygen annealing results in both the excess hole doping of CuO$_2$ layers and in the formation of some mesoscopic defects that display a paramagnetic behavior.

**Acknowledgements**

I would like to thank of Prof. P.H. Kes for the ongoing research collaboration with Kamerlingh Onnes Laboratory. I would also like to thank Roel J. Drost for his effort on SQUID measurements. I wish to thank the Department of Chemistry at the University of Marmara-Istanbul for the use of their furnace.

**References**

III.2.4. Some critical aspects of quenched melt growth
HgBa$_2$Ca$_2$Cu$_3$O$_x$ crystals
International Cryogenic Materials Conference, ICMC 2000, Rio de Janeiro, Brazil
11-15 June 2000

Ülker Onbaşlı
University of Marmara, Fen-Ed. Fak. Ziverbey 81040, Istanbul-Turkey

Abstract

Mercury based superconducting oxides were fabricated by a unique melt textured process, called QMG (quenched melt growth) technique. The optimally oxygen doped and over doped QMG bulk superconductors with zero resistance of 136K and 126K from magnetic measurements, are expected to realize new applications, because of their high critical current density $J_c$, and that the irreversibility lines. Analysis of critical currents, deduced from dynamic hysteresis loops, was made in the frame of the Bean Critical State model by working below the lower critical field value (by means of solely diamagnetic region). The optimally oxygen doped, QMG Hg-1223, have very high critical current densities, $J_c=3.75 \times 10^7$ A/cm$^2$ at 4.2K and 1T. $J_c=1.25 \times 10^6$ A/cm$^2$ at 77K and 0.25T. Further annealing of optimally doped samples in oxygen atmosphere at 300$^0$C, resulted in about two order of magnitude decrease for both of the critical current, $J_c$ and upper critical field, $B_{c2}$ at 77K. By varying the temperature from 5K to 77K, $J_c$ values of the over doped samples were found to decrease from $\sim 10^7$ A/cm$^2$ to $\sim 10^4$ A/cm$^2$, whereas, $B_{c2}$ dropped from 0.49 T to 0.07T at above-mentioned temperatures.

1. Introduction

Mercury based superconductors have inspired many researchers, not only for their high critical temperatures $T_c$, but also for having very high critical current densities, $J_c$ and irreversibility lines. Polycrystalline mercury cuprates were first synthesized by using the solid-state reaction technique (SSRT) [1-2]. Three years after the discovery of the mercury-based copper oxides, it was determined by both magnetic susceptibility and resistivity measurements
that, HgBa$_2$Ca$_2$Cu$_2$O$_{8+x}$ (Hg-1212) - HgBa$_2$Ca$_2$Cu$_3$O$_{8+x}$ (Hg-1223) polycrystalline mercury cuprates have the highest-Meissner transition temperatures of 138 K at atmospheric pressure [3]. By introducing some pinning centers into high temperature superconductors, the critical current and that of the irreversibility line can be improved. Furthermore, the unique quenched melt growth (QMG) method, that enables us controlling of the phase diagram of the oxide superconductors, in such a way to provide some additional pinning sites to them.

To improve the critical current density, Jc values and that to move the irreversibility line to higher temperatures, the quenched melt growth method, (QMG) was used for preparation of Hg-1223 superconductors with T$_c$=136 K for the first time [4]. In this work, the effect of some additional heat treatments and that the oxygen doping on the intragranuler critical current, Jc and the upper critical field, Bc$_2$ of the QMG Hg-1223 samples have been investigated. The critical current densities, deduced from dynamic hysteresis loops, at 4.2 K, and 77 K, which were calculated in the frame of the Bean Critical State model [5]. The grain size of the Hg-1223 samples was found from SEM measurements. By using the random intercept method the grain size was determined to be about 5 μm (Section III.2.2, Figure 1).

Using melt textured growth (MTG) process for YBaCuO, the weak link problem was first solved by Jin et al [6]. By introducing the pinning centers into bulk YBaCuO, Jc values have been improved and have reached to $10^4$-$10^5$ A/cm$^2$ at 77 K in magnetic fields of several tesla [7-9].

In this work, the study of the unique feature observed on QMG Hg-1223 samples, the effect of strong surface pinning at low temperatures over a wide range of magnetic fields up to 5 T has been reported. Furthermore, the process of QMG and optimal oxygen doping provided some intrinsic bulk pinning centers, without surface barrier pinning at high temperatures (The related M-H curves have been given in Section III.2.2, Figure 2 and Figure 3).

Further annealing of the samples in oxygen, resulted in decrease of the critical current and that the upper critical field values of the Hg-1223 superconductors at 5K and 77K (Figure 1 and Figure 2).

When dealing with melt process superconductors such as YBaCuO, it was experimentally determined by Murakami [10] that the magnetization of the samples was found to be independent of the sample thickness indicating
Figure 1. Magnetization $M$ versus applied magnetic field $H$, ($M$-$H$) curve of post oxygen annealed QMG Hg-1223 sample at 5K.

Figure 2. Magnetization $M$ versus applied magnetic field $H$, ($M$-$H$) curve of post oxygen annealed QMG Hg-1223 sample at 77K.
that shielding currents are localized within the individual grains. An identical effect has been observed in our laboratory the Hg-1223 samples and we have attributed that the state of current loop is represented by the average size (t) of the grains.

2. Experiment

The quenched melt HBCCO materials were synthesized using two step procedure. At the first step, the nominal composition Ba₂Ca₂Cu₃Oₓ, prepared using four nine purity of BaO, CaO, CuO, heated at 1340 °C in oxygen for 10 h. The melt starting material, BCCO was quenched in the vapour of liquid nitrogen, was removed from the gold crucible, and ground in a glow box with use of argon atmosphere. Rest of the first step, such as pressing of well ground powder BCCO into pellets and placing it in one end open quartz tube was carried out in air. The reactant material, high purity HgO put in a smaller diameter test tube, and was placed in (15 cm long) the first tube, which was finally evacuated and sealed. At the second step, the sealed tube was put horizontally in a furnace and heated at a rate of 1.5 °C/min. to 940 °C for 3 h. Due to decomposition pressure of HgO, the pressure inside the tube raised up to several hundred bars. It was cooled at a rate of 0.5 °C/min. Finally, Hg-1223 superconducting materials were annealed at 300°C temperature well below the decomposition temperature of HgO, for 10 h.

Both dc magnetic susceptibility and the dynamic hysteresis measurements were performed by the Quantum Design SQUID Susceptometer, model MPMS-5S. For the dc susceptibility measurements the magnetic field of 10⁻³ T was applied to the samples. The same swept rate of 0.025 T/s was used for the hysteresis measurements performed at various temperatures. With respect to the Bean Critical State approach, the J_c values which have been deduced from M-H curves and calculated by eq. (1). Referring to the SEM picture given in Section III.2.2 using random intercept method, the average grain size t in eq. (1) was determined as 1.5 μm.

The critical current densities J_c, were calculated with respect to the Bean Critical State model, for the applied magnetic field H parallel to c-axis H/C, the critical current J_y flows in the ab-plane of the sample. The calculation of J_c’s are made just below the lower critical field Hc1 at which the system expels the applied magnetic field entirely.
In the critical state $J_c$ is written as: $J_c \propto \frac{\Delta M}{t}$

Where, $\Delta M$ is the difference in magnetization between the increasing and the decreasing field branches, and $t$ is the average grain size. From Fig. 1 given in Section III.2.2, $t = 1.5 \, \mu m$. From hysteresis measurements we determined the critical current densities of optimally oxygen doped, QMG mercury cuprate samples that flows in the a-b plane, $J_c = 6.53 \times 10^7 \, A/cm^2$ at 4.2 K and 0.25 T (Fig. 2 in Section III.2.2). The same calculation was made at 77 K and 0.25 T, resulting $J_c = 1.25 \times 10^6 \, A/cm^2$, (Fig. 3 in Section III.2.2). For the higher fields up to 1 Tesla, the critical current density of the sample was found to be $3.75 \times 10^7 \, A/cm^2$ at 4.2 K.

3. Results and discussion

We first addressed the fact that to improve $J_c$ without having any grain boundary weak-link problem at high temperature $T > 77K$, the QMG process can be successfully used for the Hg-1223 bulk superconductor.

It was previously determined that the unique QMG technique provided us with non degrading very dense, rigid superconducting mercury cuprate material with a very high transition temperature of 136K [4].

In this work, both the melt technique and appropriate oxygen annealing were found to be very important in stabilizing the Hg - cuprate samples prepared at about atmospheric pressure.

Referring to Fig. 2 in Section III.2.2, the hysteresis measurements made at 4.2K which displays very asymmetric hysteresis loops with respect to increasing versus decreasing field branches, where both a strong surface effect and bulk pinning occur. Fig. 3 given in Section III.2.2 displays the symmetric hysteresis loops with respect to increasing versus decreasing field branches where a weak surface effect occurs and bulk pinning dominates. By combining the result obtained from the hysteresis loops, it is seen that as the temperature increases so the weak- link between the grains decreases. This behaviour can be easily understood by recalling the thermally assisted flux flow model (TAFF) in HTS oxides [11].

Hence, at higher temperatures $T \geq 77K$, the surface pinning vanishes whereas bulk pinning dominates for QMG mercury cuprates. One further
point is that the unpaired Cu$^{+2}$ ions and/or some mesoscopic defects give rise to the paramagnetic tendency of the samples at high applied field values. From Fig. 2 and Fig. 3 shown in Section III.2.2, it is seen that this behavior starts beyond 3T at 4.2K and that 1.5T at 77K for the QMG mercury cuprates.

Nevertheless, the paramagnetic behavior of the hysteresis curves and weak surface pinning have been previously observed by Niderost et al. and Mota [12] in Bi$_2$Sr$_2$CaCu$_2$O$_x$ single crystals at low temperatures and by Murakami[13] for melt processed rare earth – Ba – Cu – O samples at 77 K.

Referring to Figure 1 and Figure 2, further annealing of optimally doped samples in oxygen atmosphere, resulted in about two order of magnitude decrease of both the critical current, $J_c$, and the upper critical field $B_{c2}$, at 77K. By varying the temperature from 5K to 77K, $J_c$ was found to decrease of about three order of magnitude, whereas, $B_{c2}$ by reduced of 86%.

As it was previously explained by Hofer et al. [14] for oxygen annealed HgBa$_2$CuO$_x$ microcrystals at which the decrease in the critical parameters has been attributed to the probable change in effective mass anisotropy, caused by the change in polaron binding energy of the mercury cuprate crystals. The effect of oxygen annealing on Hg -1223 thin films was also investigated by Kang et al. [15], and the critical current density of about $10^7$ A/cm$^2$ at 10 K was observed on the thin films.

Hence this work is related to the high Tc superconductor prepared in our laboratory which is thermally stable at $T \geq 90$K. As a conclusion, QMG mercury cuprates have been proposed to be used for various technological applications where liquid oxygen has a particular function.

Acknowledgment

I wish to thank to the department of Chemistry at University of Marmara-Istanbul for the use of their furnace. I would like to thank P.H. Kes and V.Kresin for many helpful discussions. I would also like to thank to R.J.Drost for his effort on squid measurements performed at Kamerlingh Onnes Laboratory.

References

III.2.5. Irreversibility line of quenched melt growth mercury cuprates
5th European Conference on Applied Superconductivity EUCAS, Copenhagen, Denmark, 26-30 August 2001

Ülker Onbaşlı
University of Marmara, Fen-Ed. Fak. Ziverbey 81040, Istanbul, Turkey

Abstract

Determination of irreversibility line of high temperature superconducting materials, HTSCs is an important problem from point of view of application. Referring to magnetization versus magnetic field, $M-H$ data of the quenched melt growth, QMG mercury cuprate, Hg-1223 crystals the problem becomes more complicated since they display a paramagnetic behaviour at relatively high magnetic fields. The paramagnetic tendency of the Hg-1223 crystals starts at 3T and 4.2K, at 1.5T and 77K. Moreover, no transition from vortex solid to vortex liquid phase was observed for a wide range of temperature, 4.2-120K in classical manner. The paramagnetic behaviour of the QMG crystals was attributed to another equilibrium state that is carrying spontaneous orbital currents resulting in corresponding paramagnetic moments at relatively high fields. Furthermore, this state is associated with the mesoscopic defect structure rather than being an intrinsic property of the ideal HTSC crystals.

1. Introduction

Multi-layered oxide superconductors have inspired many researchers, due to their high critical parameters of Meissner transition temperature, $T_c$, critical current density, $J_c$, and irreversibility field, $H_{irr}$. Determination of the irreversibility line of high-Tc superconductors is very important for some technological applications since above the irreversibility field, the fluxoids form no lattice and move freely, that results a transition from a vortex glass to a liquid leading to a thermally driven depinning. In most experimental work, the irreversibility line is determined by a mobility criterion for the vortex lattice [1]. The aim of the study is to determine the irreversibility field, $H_{irr}$, of the melt textured mercury cuprate superconductors HgBa$_2$Ca$_2$Cu$_3$O$_x$, (HBCCO) over the temperature range of 4.2-120K. From dynamic hysteresis
measurements, $\Delta M$ versus magnetic field curves were drawn and $H_{irr}$ was determined when magnetization curve has no longer doubled value, $\Delta M=0$. Since HBCCO is a type II superconductor, there are vortices above a critical field $H_{c1} \leq H \leq H_{c2}$. This condition ensures that $\xi \leq R \leq \lambda$ where $\xi$, $R$ and $\lambda$ are the coherence length, vortex radius and penetration depth, respectively. Around each vortex, there is a rotating superfluid condensate. Quasi-particles are excited out of this condensate. In addition, the individual quasi-particles have a paramagnetic response to the applied magnetic field due to their intrinsic spin and we refer to this as the paramagnetic effect (PE). Paramagnetic behavior of the hysteresis curves and weak surface pinning have been previously observed by Niderost [2] in Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ single crystals at low temperatures and by Murakami [3] for melt processed rare Earth-Ba-Cu-O superconducting samples at 77K. Furthermore, Tafuri and Kirtley [4] reported the spontaneous magnetization in YBa$_2$Cu$_3$O$_x$ thin films. This is qualitatively similar to that seen [5] in granular BSCCO samples which show the paramagnetic Meissner (Wohlleben) effect. In this work, the quenched melt growth method, QMG used for preparation of mercury cuprate bulk material. Apparently, the method improves the irreversibility line and move to higher temperatures, by some additional treatment of the material. Using melt textured growth (MTG) process for YBaCuO, the weak link problem was first solved by Jin et al. [4]. By introducing the pinning centers

![Figure 1. Magnetization, $M$ versus applied magnetic fields, $H$ of the Hg-1223 superconductors at 4.2K, 27K and 77K.](image-url)
into bulk YBaCuO, $J_c$ values have been improved and have reached $10^5$ A/cm$^2$ at 77K in the magnetic field of several Tesla [5-7]. Nevertheless, providing additional pinning sites to oxide superconductors made controlling of the phase diagram of the system very difficult as well as the usage of the material for particular applications. In this work, we report the study of the unique feature observed on QMG Hg-1223 samples, the effect of strong pinning at low temperatures over a wide range of magnetic fields up to 5T. Furthermore, the process of QMG provided some intrinsic bulk pinning centers without surface barrier pinning at liquid nitrogen temperature (Figure 1). When dealing with melt process superconductors such as YBaCuO [8], it was experimentally determined that the magnetization of the samples was found to be independent of the sample thickness indicating that shielding current are localized within the individual grains. An identical effect has been observed by us on the Hg-1223 samples and we have assured that the state of current loop is represented by the average size of grains.

2. Experimental

The mercury cuprate bulk samples, Hg-1223 have been prepared by the quenched melt growth method using four nine purity materials of BaO, CaO, CuO and HgO. The quenched melt HBCCO materials were synthesized applying two step procedure. At the first step, the nominal composition of Ba$_2$Ca$_2$Cu$_3$O$_x$, prepared using the high purity oxides, heated at 1340$^0$C in oxygen for 10h. The melt starting material, BCCO was quenched in the vapor of liquid nitrogen, was removed from the gold crucible, and ground in a glow box with use of argon atmosphere. Rest of the first step, such as pressing of well ground powder BCCO into pellets and placing it in one end open quartz tube was carried out in air. The reactant material, high purity HgO put in a smaller diameter test tube, and was placed in (15cm long) the first tube, which was finally evacuated and sealed. At the second step, the sealed tube was put horizontally in a furnace and heated at a rate of 1.5$^0$C/min to 940$^0$C for 3h. Due to decomposition pressure of HgO, the pressure inside the tube raised up to several hundred bars. It was cooled at a rate of 0.5$^0$C/min. Finally, Hg-1223 superconducting materials were annealed at 300$^0$C temperature well below the decomposition temperature of HgO, for 10h.
The dynamic hysteresis measurements were performed by Quantum Design SQUID Susceptometer, model MPMS-5S. The same sweep rate of 0.025T/s was used for the hysteresis measurements performed at 4.2K, 27K, 77K and 120K. According to dc magnetic susceptibility measurements, it was previously determined that the Meissner onset temperature was $T_c=136K$ [11]. The difference in magnetization between the increasing and decreasing applied field branches, $\Delta M$ was deduced from Figure 1 and the data extracted was used to draw log-log plot of $\Delta M$ versus applied magnetic field, $\Delta M - H$. Figure 2 shows that $\Delta M$ decays rapidly with increasing temperature from 4.2K to 77K. At low temperatures, $\Delta M$ decreases exponentially and decays linearly at liquid nitrogen temperature.

$H_{irr}$, as determined from the vanishing of $\Delta M$ and follows an exponential decay law;

$$H_{irr} (T) \approx \exp \left( \frac{T}{T_c} \right)$$

where $T/T_c$ is the normalized temperature, $T_c=136K$ (Figure 3).

**Figure 2.** Log $M$–Log $H$ plot of the mercury cuprates for $H//c$. 
3. Results and discussion

We first report the fact that the unique QMG technique provided us a non-degrading very dense, rigid superconducting mercury cuprate material with Meissner transition temperature of 136K. Furthermore, both the melt technique and appropriate oxygen annealing were found to be very important in stabilizing the Hg-cuprate samples prepared at atmospheric pressure. This result has been confirmed by dc-SQUID measurements performed on Hg-1223 samples which have been kept in air for several months after being synthesized. Referring to the $M-H$ curves, it was determined that the superconducting mercury cuprates were thermally stable up to 120K. The rapid decay of $\Delta M$ with temperature was attributed to the indication for substantial thermally activated flux motion [12]. Magnetic hysteresis, due to pinning was scaled between 4.2K and 120K suggesting that the results are not based on a single pinning mechanism over this temperature range. Moreover, a temperature dependent crossover is not favored since that the paramagnetic tendency starts at relatively low temperature of 4.2K. The paramagnetic response is strikingly contrast to the diamagnetic behavior which is a
hallmark of superconductivity. It has been argued that the paramagnetic Meissner effect (PME) results from a d-wave symmetry in the cuprate superconductors order parameter [13]. More likely that the superconductivity in optimally oxygen doped mercury cuprate superconductors can be characterized by an orbital component of the pairing wave function with predominantly $d_{x^2-y^2}$ symmetry. The $d_{x^2-y^2}$ order parameter does not violate time-reversal symmetry. Nevertheless, it has been theoretically shown that broken time-reversal symmetry (BTRS) could occur locally in $d_{x^2-y^2}$ superconductor at certain surfaces and interfaces or in the presence of nonmagnetic impurities [14-19]. Moreover, as was previously observed on many other CuO-layered superconductors, such as YBCO, BSCCO, (Er$_{0.8}$Ca$_{0.2}$)Sr$_2$(Ti$_{0.5}$Pb$_{0.5}$)Cu$_2$O$_x$, HBCCO displaying PME around the transition temperature [20-23]. Since this magnetization appears spontaneously suggesting another equilibrium state associated with the mesoscopic defects rather than being an intrinsic property of ideal HTSC crystals. The paramagnetic behavior of the QMG crystals was attributed to another equilibrium state carrying spontaneous orbital currents that results in corresponding paramagnetic moments at relatively high fields.

$H_{tr}$ is relatively higher for Hg-based cuprates [24] than the other oxide superconductors. Furthermore, QMG method provides some possible unpaired Cu$^{+2}$ ions that act as paramagnetic sites resulting in samples which do not exhibit any upper critical field $H_{c2}$ in a classical manner [11]. Because of the fact that the content of the unpaired Cu$^{+2}$ ions can be controlled by the method of preparation in such as way giving rise to the irreversibility line which in turn leads QMG Hg-cuprates being safely used for high temperature, high field applications.

4. Acknowledgements

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References

III.2.6. Symmetry breakings and topological solitons in mercury based d-wave superconductors

Ülker Onbaşlı1#, Zeynep Güven Özdemir2, Özden Aslan3
1Department of Physics, University of Marmara, Ridvan Pasa Cad. 3. Sok. 85/12 Goztepe, Istanbul
2Department of Physics, Yildiz Technical University, Davutpasa Mah. Davutpasa Caddesi 34220 Esenler-Istanbul Turkey
3Anatürkler Educational Consultancy and Trading Company, Orhan Veli Kanik Cad. Güner İş Mer., 6/1, Kavacık 34810 Beykoz, Istanbul, Turkey

Abstract

This study is devoted to examine high temperature superconductors by the concept of symmetry breakings. The global gauge symmetry is broken at Meissner transition temperature, $T_c$, in high temperature d-wave superconductors. In addition to this symmetry breaking, the time reversal symmetry breaking phenomenon becomes observable on Paramagnetic Meissner Effect at Paramagnetic Meissner effect temperature, $T_{PME}$. Furthermore, the concept of symmetry breakings has been discussed by the phenomenon of critical quantum chaos in the mercury cuprates which is one of the best examples to understand the chaotic transitions. From this point of view, $T_c$ and $T_{PME}$ have been suggested as chaotic transition points. Moreover, $T_{PME}$ is predicted as the breaking point of electroweak symmetry as well. Furthermore, we have also proposed that the double helix quantum wave occurs in the quantum primitive cell of cuprates due to the breaking of the room temperature symmetry of the system at $T_c$. When time period of the wave is taken infinite, the double helix quantum wave can be considered as a topological soliton of the coherent system.

1. Introduction

The concepts of the symmetries and symmetry breakings are accepted as one of the most unresolved problems of the 21st century. The symmetries have a crucial role in giving information about the present forces in a system considered and that symmetries can be broken in various ways such as variation of density, temperature, etc. [1].

#Correspondence/Reprint request: Prof. Dr. Ülker Onbaşlı, Ridvanpaşa cad., 3.Sok., 85/12, Göztepe 34730 Istanbul, Turkey. E-mail: phonon@doruk.net.tr; zguvenozdemir@yahoo.com
The simplest way of explaining various phenomena in nature is based on the investigation of the symmetry concept. For example, the concepts of the conservation of energy and momentum, being essential for conservation laws of physics, are fundamental results of the symmetries of time and space, respectively. Furthermore, understanding of fundamental forces such as gravitation, electromagnetic, weak and strong nucleus forces are based on the related local gauge symmetries [2].

The superconductors, in which phonon mediated attractive electron-electron interaction leads to formation of quasi-particles, namely Cooper pairs, constitute a natural laboratory for searching and determining the quantum critical chaos points. In this study, symmetries and their breakings have been investigated via the critical quantum chaos points in mercury based layered cuprate superconductors that have the highest Meissner transition temperature at normal atmospheric pressure [3].

2. Symmetry groups and symmetry breakings in superconductors

The transition from normal state to superconducting state occurs at Meissner transition temperature, \( T_c \). The Meissner transition temperature can be referred to as the formation of \( d_{x^2-y^2} \)-wave symmetry in cuprates. In other words, the room temperature symmetry (non-superconducting phase) of the cuprate superconductor is broken at \( T_c \) so that the superconductor is \( d \)-wave symmetric below \( T_c \).

Since a transition to superconducting state is a second order phase transition, the symmetry breaking is continuous in the system [4,5]. The continuous symmetry breaking corresponds to spontaneous symmetry breakings in the superconducting state. Furthermore, as stated by El Naschie in the E-Infinity Theory, topology of quantum space-time is changed during the symmetry breaking [6].

According to group theory, the symmetry group \( H \) describing the superconducting state must be a subgroup of the full symmetry group \( G \) describing the normal state.

\[
G = X \ast R \ast U(1) \ast T \ast I \quad \text{for normal state (} T \geq T_c \text{)}
\]

\[
H \subseteq G \quad \text{for superconducting state (} T \leq T_c \text{)}
\]
where, \( X \) is the crystallographic point symmetry group, \( R \) is the symmetry group of spin rotation, \( U(1) \) is one dimensional global gauge symmetry corresponding to the spin momentum symmetry, \( T \) is the time reversal symmetry operation associated with orbital momentum symmetry, and \( I \) is the inversion operation [7-9]. More detailed information about these symmetries and their breakings are as follows:

a) Crystallographic point group symmetry

The crystal structure of cuprates can be divided into two categories for this symmetry: I) Tetragonal lattice with \( D_{4h} \) point group symmetry II) Orthorhombic lattice with \( D_{2h} \) point group symmetry. Some cuprates such as \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \), \( \text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8 \), \( \text{HgBa}_2\text{CaCu}_2\text{O}_6 \) (Hg-1212), and \( \text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x} \) (Hg-1223) have the tetragonal crystal structure [7,8,10].

b) Spin rotation symmetry

This symmetry is broken in the magnetically ordered system which has the phase coherence [11]. It is known that, the spin-orbit coupling is very weak in ceramic superconductors and the wave function of electron pairs with even parity is in the spin singlet state (\( S=0 \)) in which the spins of electrons have opposite direction. The wave function of electron pairs with odd parity is in the spin-triplet state (\( S=1 \)) [7].

c) One dimensional global gauge symmetry, \( U(1) \)

This symmetry is broken together with order parameter in the superconducting state due to the off-diagonal long range order [12]. In the unconventional superconductors, in addition to global gauge symmetry, one or more symmetries can be broken in the superconducting state [7].

d) Time reversal symmetry

In the unconventional superconductors, the breaking of the time reversal symmetry is related to the orbital magnetism and vortex. This symmetry can be destroyed under applied magnetic field and magnetic impurities [13]. In literature, it has been predicted that the time reversal symmetry breaking occurs below Meissner transition temperature, \( T_c \) [14]. Furthermore, it has
been proposed that a novel thermodynamic phase called “chiral-glass phase” may occur in zero external field in some ceramic high $T_c$ superconductors. The chiral-glass phase is characterized by a spontaneously broken time reversal and one dimensional global gauge symmetry [15].

In this study, it is suggested that the Paramagnetic Meissner Effect (PME) refers to the concept of the time reversal symmetry breaking in mercury cuprates. Furthermore, since the time reversal symmetry is broken at $T_{PME}$ in mercury cuprates, the superconducting system can be considered in the chiral-glass phase. Moreover, this symmetry breaking phenomenon has been discussed using the quantum mechanical approach in the context of PME and electroweak symmetry breaking phenomenon in Section 4.4 and 6.3, respectively.

e) Inversion symmetry

Due to spatial inversion, the spin-singlet pair wave function ($\psi^s$) is the same under the inversion symmetries, $I\psi^s = \psi^s$, whereas the spin-triplet pair wave function ($\psi^t$) changes its sign, $I\psi^t = -\psi^t$ [7,8].

Similar to superconducting transition, the concept of the chaos can be defined as the transition from one state of order to another where the probability density of the system, which is sensitive to the initial conditions, changes via temperature [16]. The phenomenon of the critical quantum chaos is observed in the quasi periodic systems, the systems with two interacting electrons and the fractal matrices [16-18]. In this context, a system of phonon mediated interacting electrons namely superconductor, in which the spontaneous symmetry breakings occur, is one of the best examples to understand the unexpected chaotic transitions.

3. Paramagnetic Meissner effect- a useful tool to detect time reversal symmetry breaking

The Meissner effect, which is the occurrence of flux expulsion below the superconducting transition temperature and the resulting diamagnetic response to the external magnetic field, is the fundamental property of superconductivity. Contrast to this diamagnetic behavior, some high temperature superconductors acquire a net paramagnetic moment when cooled in a small magnetic field. This effect is known as the Paramagnetic Meissner Effect (PME or Wohlleben Effect) [3,19-24]. The PME leads to
spontaneous currents in opposite direction with diamagnetic Meissner current in superconductors that result in the breaking of time reversal symmetry.

The PME can only be observed in single crystals such as Nb, Al etc. [7] and some cleanly prepared polycrystalline samples such as YBa$_2$Cu$_3$O$_{7-x}$ [21], Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ [22, 25]. The PME has also been observed on very cleanly prepared Hg-cuprate samples [3]. In high $T_c$ superconductors, the possible mechanisms of the PME are the spontaneous orbital currents (negative supercurrent i.e. orbital moments) due to $\pi$-junctions and vortex pair fluctuations combined with pinning in d-wave superconductors [23]. Moreover, the mechanism of the PME is based on the phase coherent coupling of superconductors that convincingly shows the order parameter with the $d_{x^2-y^2}$ wave symmetry [26]. According to Heinzel et al., the PME state carrying spontaneous orbital currents results in corresponding paramagnetic moments that can be reversibly aligned under small external dc fields [27].

In this study, the origin of the PME can be considered as the spontaneous direction change of the orbital currents in mercury cuprates. In section 4.4, the PME has been attributed to the time reversal symmetry breaking phenomenon due to the development of a conceptual relation between change of the direction of magnetic moment and magnetic quantum number.

4. Experimental investigation of PME in mercury cuprates by means of symmetry breakings and chaotic transitions

4.1. Preparation of optimally oxygen doped HgBa$_2$Ca$_2$Cu$_3$O$_{8+x}$

In this study, the PME has been examined by alternative current magnetic measurements of optimally oxygen doped HgBa$_2$Ca$_2$Cu$_3$O$_{8+x}$ (Hg-1223) superconducting sample, which has the highest Meissner transition temperature of 140K (a new world record of $T_c$) at normal atmospheric pressure.

The HgBa$_2$Ca$_2$Cu$_3$O$_{8+x}$ (Hg-1223) superconductors were synthesized using two step procedure. In the first step, the nominal composition Ba$_2$Ca$_2$Cu$_3$O$_x$ (reactant material), prepared using four nine purity of BaO, CaO, CuO, heated at 1340°C in oxygen environment for ten hours. Ba$_2$Ca$_2$Cu$_3$O$_x$ was quenched in the vapour of liquid nitrogen, removed from the gold crucible, and grounded in a glow box under argon atmosphere. Following operations of pressing well ground powder Ba$_2$Ca$_2$Cu$_3$O$_x$ into a pellet and placing it in a one end open quartz tube (first tube) were carried out in air. The reactant material, the high purity HgO, which was put in a smaller
diameter test tube, were both placed in the first tube, which was finally evacuated and sealed. In the second step, the sealed tube was placed horizontally in a furnace and heated at a rate of 1.5°C/min. to 940°C for three hours. Due to decomposition pressure of HgO, the pressure inside the tube raised up to several hundred bars. In order to protect the furnace from possible hazardous effects, these two tubes are put in a closed stainless-steel protecting tube. It was cooled at a rate of 0.5°C/min. In order to obtain the optimally doped Hg-1223 superconducting material, the sample was annealed in oxygen atmosphere at 300°C, well below the decomposition temperature of HgO, for ten hours. Eventually, the concept of the optimal oxygen doping procedure has been defined by referring to the Meissner critical transition and paramagnetic Meissner temperatures obtained from the magnetic moment versus temperature data of the superconducting sample.

4.2. Magnetic measurements

Magnetic measurements were performed by the Quantum Design Superconducting Quantum Interference Device (SQUID) magnetometer; model MPMS-5S, under a weak alternative current magnetic field of 1 Gauss with 1kHz. The real and imaginary components of the magnetic moments of the superconducting sample are presented in Fig. 1a. It can be seen that the imaginary component of magnetic moment, which corresponds to the maximum of the PME, occurs and decreases to saturation in the temperature range of about 15K for optimally oxygen doped Hg-1223. Moreover, this paramagnetic moment manifests itself as the sample is cooled about 5K below Tc (140K) and then saturates for optimally oxygen doped mercury cuprates. From the mathematical point of view, magnetic moment curves are constant and the real part of magnetic moment has a value of zero, so the sample is in the normal phase above 140K.

4.3. Determination of symmetry breakings and chaotic transitions

Some symmetry breakings of Hg-1223 have been determined by applying two analyzing steps on PME data. All results have been combined to predict the temperatures at which the symmetries are broken.

In the first step of analyzing, some special temperature values have been determined from the magnetic data by the derivation of magnetic moment with respect to the temperature. Since there is no entropy propagation in superconductors, the only variable in the superconducting state that drives the
Figure 1. The magnetic moment data of Hg-1223 sample. (a) The real and imaginary parts of the magnetic moments. Regions are separated by some special temperature values obtained from Fig.1 b. (b) The first derivative of the real and imaginary parts of the magnetic moment.

The entire process of the PME is the temperature. From this point of view, all derivatives have been taken with respect to temperature. After the calculation of the first derivative of the real and the imaginary parts of magnetic moment data, special temperature values (103K, 122K and 135K) have been found as shown in Fig. 1b [28]. According to Fig. 1a and Fig. 1b, the PME temperature, $T_{\text{PME}}$, has been determined as 122K. The magnetic moment data is divided into four temperature regions as presented in Fig. 1a according to these temperatures, each temperature region corresponds to existence or non-existence of particular symmetries that are time reversal and d-wave symmetries.

It was surprisingly found that the temperature dependences of the real ($m'$) and imaginary ($m''$) magnetic moment components, which have been determined by the Origin Lab 7.5 graphic program, have the same
Mercury based high temperature superconductors

mathematical forms but different fitting parameter values in each region. Moreover, at 122K, while the directions of spins change, the mathematical functions change their forms from exponential to Gaussian. The fitting functions and fitting parameters of the temperature dependence of \( m' \) and \( m'' \) for Region 2 are given in Eq. (1).

Region 2 (103-122K)

\[
m' = m_0' + A e^{(T-T_0)/T_1} \quad \text{(Exponential form)}
\]

\[
m_0' = -0.0016 \text{emu} \quad T_0 = 8.85797K \quad A = 2.6907 \times 10^{-16} \text{emu} \quad T_1 = 3.95038K
\]

\[
m'' = m_0'' + A e^{(T-T_0)/T_1} \quad \text{(Exponential form)}
\]

\[
m_0'' = 0.00012 \text{emu} \quad T_0 = -84.27K \quad A = 2.92 \times 10^{-30} \text{emu} \quad T_1 = 3.51381K
\]

The fitting functions and fitting parameters of the temperature dependence of \( m' \) and \( m'' \) for Region 3 are given in Eq. (2).

Region 3 (122-135K)

\[
m' = m_0' + \frac{A}{w\sqrt{\pi}/2} e^{-\frac{2(T-T_0)^2}{w}} \quad \text{(Gaussian form)}
\]

\[
m_0' = -1.7449 \times 10^{-6} \text{emu} \quad T_0 = 109.02752K \quad A = -0.09729 \quad w = 13.15772
\]

\[
m'' = m_0'' + \frac{A}{w\sqrt{\pi}/2} e^{-\frac{2(T-T_0)^2}{w}} \quad \text{(Gaussian form)}
\]

\[
m_0'' = 0.00002 \text{emu} \quad T_0 = 122.14107K \quad A = 0.001887 \text{emu} \quad w = 5.23167
\]

The second step in analysis was the calculation of the phase difference, \( \phi \), between real \( (m') \) and imaginary \( (m'') \) components of magnetic moments. These components are related to magnetic moment \( m \) and \( \phi \) as given in Eq. (3).

\[
m = \sqrt{m'^2 + m''^2}
\]

\[
m' = m \cos \phi
\]

\[
m'' = m \sin \phi
\]

\[
\phi = \arctg \left( \frac{m''}{m'} \right)
\]
The phase difference versus temperature graphic, obtained from Eq. (3), is given in Fig. 2.

Let us examine each region of Fig. 1a and Fig. 2 in the view of symmetry concept. Meissner transition temperature of 140K is referred to as the phase coherence and it is the beginning point of superconductivity for the optimally oxygen doped Hg-1223 superconductor investigated. Furthermore, the critical temperature, $T_c$, marks a phase transition where the one dimensional global gauge symmetry is spontaneously broken. One dimensional global gauge symmetry breaking manifest itself as the $\pm \pi / 2$ phase jumping in the vicinity of $T_c$ in phase difference versus temperature graphic as illustrated in Fig. 2. From this point of view, the Meissner critical temperature, $T_c$, refers to the first chaotic transition point since the system is in a new ordered state below $T_c$ [29]. Moreover, the system becomes d-wave phase symmetric superconductor below 140K for the samples mentioned above.

In the normal state, time reversal symmetry (TRS) does exist. In the temperature region from 135 to 122K, the system has d-wave symmetry and TRS. The PME temperature of 122K has a particular meaning as the imaginary component of magnetic moment starts to change its direction. From the quantum mechanical point of view, the situation manifests itself as the occurrence of spontaneous orbital currents resulting at PME temperature. In other words, PME temperature can be considered as the second chaotic transition point of the superconducting system due to the breaking of time reversal symmetry [29].

![Figure 2. The phase difference versus temperature of Hg-1223 sample in between 70-145K.](image)
In region 3, real and imaginary components of the magnetic moment both obey Gaussian distribution as given in Eq. (2). By decreasing the temperature from the PME temperature to 103K, the superconducting system displays an exponential decay as given in Eq. (1). Therefore, the PME temperature of 122K ($T_{PME}$) corresponds to the time reversal symmetry breaking point. More detailed quantum mechanical explanation of the relationship between the time reversal symmetry breaking and the PME in mercury cuprates has been presented in Section 4.4. As given in Fig. 1a, the temperature region of the observed maximum paramagnetic signal is considered as the chiral-glass phase due to spontaneous time reversal symmetry breaking. From this respect, the formation of the chiral-glass phase at $T_{PME}$ can be considered as the second chaotic transition in the Hg-1223 superconducting system [29].

By keeping on decreasing the temperature, both BTRS and phase symmetries exist. Since the phase difference between real and imaginary components of the magnetic moment is almost constant from 120 to 70K, the BTRS persists in regions 1 and 2 as well. As shown in Fig. 2, the phase angle starts to change above 140K. This change can be considered as the decay of phase difference. The phase difference, $\phi$, versus temperature curve gives a phase difference of $180^\circ$ at about Meissner transition temperature. This special phase difference value can be considered as the beginning point of the d-wave symmetry or referred to as the breaking of the room temperature symmetry of the superconductor.

All interpretations discussed above have been summarized in Table 1.

**Table 1.** Analysis of symmetry breaking for real and imaginary magnetic moments based on the Figs. 1. and 2.

<table>
<thead>
<tr>
<th>Region</th>
<th>Temperature range (K)</th>
<th>Mathematical Forms¹</th>
<th>Symmetries</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>145-135</td>
<td>Linear form except at $T_c$</td>
<td>TRS exists (Fig. 1). One dimensional global gauge symmetry is broken at 140K. (Fig. 2).</td>
</tr>
<tr>
<td>3</td>
<td>135-122</td>
<td>Gaussian Form</td>
<td>TRS and d-wave symmetry exist. Decoy of difference appears.</td>
</tr>
<tr>
<td>2</td>
<td>122-103</td>
<td>Exponential Form</td>
<td>BTR and d-wave symmetries exist. Decay of phase difference goes on.</td>
</tr>
<tr>
<td>1</td>
<td>103-70</td>
<td>Linear form</td>
<td>BTRS and d-wave symmetries exist. Phase coherent coupling is valid.</td>
</tr>
</tbody>
</table>

¹Mathematical forms such as Gaussian distribution are obtained by the Origin Lab 7.5.
4.4. A quantum mechanical explanation to paramagnetic Meissner effect

In this study, the quantum mechanical interpretation of PME is based on the development of a conceptual relationship between the time reversal symmetry and the magnetic quantum number of the system. It is known that, reversing the time (t) not only replaces t by –t in equations, but also it reverses momentums defined by the time derivatives of spatial quantities such as angular momentum, L. Furthermore, magnetic quantum number, m, refers to the projection of the angular momentum, L_z. This component of angular momentum in z direction can be defined by the formula:

\[ L_z = m \hbar \]  \hspace{1cm} (4)

where \( \hbar (= h/2\pi) \) is the reduced Planck constant. Since, there is a relationship between the magnetic moment and magnetic quantum number, inverting the direction of the time flow will affect the z component of angular momentum, magnetic quantum number, and magnetic moment. For this reason, the magnetic moment versus temperature data in Fig. 1a has been re-examined in the context of magnetic quantum numbers as illustrated in Fig. 3. In this respect, alternative current magnetic moment versus temperature data of the optimally oxygen doped Hg-based cuprate has been proposed to explain the time reversal symmetry breaking phenomenon. In Fig. 3, magnetic moment versus temperature curve of Hg-1223 has been divided into three regions with respect to magnetic quantum number, m. Since the system investigated is represented by the d-wave with the orbital quantum number, \( \ell \), equal to 2, the m values will vary from minus two to plus two (\( \ell = 2, m = \pm 2, \pm 1, 0 \)).

The superconducting system has the room temperature symmetry (non-superconducting phase) in region III. The temperature region at which the d-wave symmetry is valid has been divided into two parts. In region II, magnetic quantum number, m, equals to \( \pm 1 \). Since the imaginary component of the magnetic moment is related to the losses of the system, the imaginary component of m in region II corresponds to the \( m = -1 \) domain. Hence the real component of m in region II corresponds to \( m = +1 \) domain. Furthermore, m is equal to minus and plus two in region I. By reducing the temperature, the magnetic quantum number of the system experiences a change from “-” to “+” and vice versa. This means that the projection of the angular momentum in z direction, L_z, passes through the zero at T_{PME}. From this point of view, T_{PME} is attributed to the breaking point of the time reversal symmetry.
Figure 3. Alternative current magnetic moment versus temperature for optimally oxygen doped Hg-1223 sample where the d-wave and room temperature symmetry regions together with the related magnetic quantum numbers (m) are indicated for three distinguished regions.

5. Double helix quantum wave as topological solitons

The order (or energy gap) parameter, $\Delta_k$, of the Hg-1223 superconductor has $d_{x^2-y^2}$-wave symmetry [30]. The gap parameter

$$\Delta_k = \Delta_0(\phi) \cos 2\phi$$

has nodes and changes its sign at every $45^0$. The terms $\Delta_0(\phi)$ and $\phi$ in Eq. (5) represent the zero-temperature value of the d-wave gap amplitude and the angle between the $x$ and $y$ components of wave vector of the paired electrons, respectively [7, 31].

Each copper oxide layer in d-wave superconductors separated by an insulating layer is a charge reservoir. This layered structure of Hg-1223 solid material and its primitive cell are given in Fig. 4. It is known that, the structural properties of copper oxide layered superconductors correspond to intrinsic Josephson junctions. Therefore, the Josephson coupling or
Figure 4. The illustrative primitive cell of Hg-1223 cuprate superconductor. The related lattice parameters obtained by X-Ray Diffraction are $a=b=3.848\text{Å}$ and $c=15.774\text{Å}$ [3].

Tunnelling among the cooper oxide layers along the c-axis has to be taken into account. The bulk superconductors can be considered as various arrays of Josephson junction unit cells (JJUC) with a phase difference of 45° [7].

A unit cell of this system with respect to d-wave symmetry is presented in Fig.5a. The schematic representation of d-wave high Tc superconductors at resonating state has been proposed in Fig. 5b. This three dimensional quantum mechanical unit cell of the d-wave superconductor contains only four JJUC and named giant Josephson junction (GJJ). The phase difference of 45° of JJUC with Josephson coupling spontaneously drives the double helix quantum waves (DHQW). In other words, DHQW is a natural and characteristic consequence of the d-wave symmetry of the copper oxide layers of cuprate superconductors at the resonating state.

Three dimensional double helix quantum structure can be attributed to the solitons as the time period of the wave is taken infinite in the phase space. We have called this intrinsic quantum waves as “Segâh Solitons” which refers to the topological solitons with respect to Cartesian space. The topological solitons are of the intrinsic properties of the superconducting copper oxide systems. Furthermore, the frequency of the DHQW, which has been roughly calculated from Fig. 5b, corresponds to ultraviolet (u.v.) region.

In this study, the Segâh solitons are proposed as the fingerprints of the mercury based copper oxide layered superconductors. For some aspects, DHQW of the superconductor and DNA of the living organism seem to
Figure 5. The structural intrinsic properties of copper oxide layered superconductors. (a) Josephson junction between two d-wave superconductors with the phase difference of 45°. (b) The predicted double helix quantum mechanical wave as appeared on the quantum mechanical unit cell of high Tc cuprates.

resemble one another. Some researchers have shown that DNA can conduct electricity and become a proximity-induced superconductor when its metal contacts become superconductor at very low temperature [32]. As human DNA is illuminated by ultraviolet, (u. v) light, this creates some excited states in DNA molecule [33-35]. It seems that the u. v frequency has an importance both in Cartesian and momentum spaces as well.

6. Discussion

6.1. Paramagnetic Meissner effect

In this study, the PME, which is considered as a fraction of overall response of superconducting samples to weak a.c. magnetic field, has been utilized as a reliable experimental tool for the investigation of time reversal symmetry breaking in high temperature superconductors. In this respect, the PME phenomenon has been suggested as a reliable method for determining broken time reversal symmetric state in superconductors instead of very
complicated experimental methods such as the angle resolved photoelectron spectroscopy (ARPS). Broken time reversal symmetry was detected in Bi-2212 superconductors by the ARPS [36]. However, using ARPS for detecting time reversal symmetry breaking phenomenon brings the possibility of having the order parameter to be collapsed by the measurement system. This might bring the question whether the non-collapsing wave function is valid in the ARPS data.

### 6.2. Double helix quantum wave

Symmetry breakings cause new disturbances in the superconducting system, such as topological solitons [37]. In this study, it has been suggested that the room temperature symmetry has broken at $T_c$ and this symmetry breaking causes the DHQW, namely Segâh Solitons, in three dimensional quantum unit cell of the system in the superconducting state. It is known that solitons are absolutely present in crystals, magnetic materials (domain walls), superconductors, super fluids (vortex), the atmosphere of the Earth and the other planets, oceans(tsunami), galaxies, and the living organism (nerve pulses) [38]. In scientific literature Solitons, which present in superconductors, are generally discussed in the context of vortex state. As is known, in type 2 superconductors, if the applied magnetic field is higher than the lower critical magnetic field of the sample, the magnetic field penetrates the sample and vortex state occurs. According to Mourachkine, these vortex can be attributed to the topological solitons that present within the long Josephson junctions and they are called as Josephson solitons [39,40]. The magnetic flux quanta (fluxon) in long Josephson junctions, which have many properties of relativistic particles with respect to limiting velocity of the light, behaves as a soliton in many cases [41,42].

In our case, the origin of the DHQW, namely the Segâh solitons, cannot be related to the vortex state or magnetic flux quanta since the applied magnetic field is only 1 Gauss, which is much lower than the lower critical magnetic field of Hg-1223. The lower critical magnetic field of Hg-1223 is in the order of 0.25T (or 2500G) at liquid nitrogen temperature [43]. Therefore, the superconducting system entirely expels the magnetic flux quanta so that the effect of vortices gets lost below $T_{PME}$ temperature.

Finally, the DHQW has been attributed to the topological solitons which conserve their properties at every temperature below $T_c$ and under any conditions as long as the d-wave symmetry is valid.
6.3. Electroweak symmetry breaking in mercury cuprates

In recent years, superconductors have been suggested as the perfect prototype for the electroweak theory and electroweak symmetry breaking due to Higgs mechanism in superconductor [44]. The Higgs mechanism in layered superconductors has been explained by Josephson plasma excitations in superconductors. The main Josephson plasma excitation modes in weakly Josephson coupled layered superconductors are longitudinal and transversal modes. The transversal Josephson plasma excitation is an electromagnetic wave propagating perpendicular to polarization to vector, k [45,46]. The related Josephson plasma frequency orders of mercury based copper oxide superconductors have already been determined as $10^{12}-10^{13}\text{Hz}$ range [43]. On the other hand, the longitudinal mode, which is known as Nambu-Goldstone (Anderson-Bogaliubov) mode, is an elementary excitation mode accompanying with the superconducting phase transition due to symmetry breaking [47-49]. The finite energy gap of superconductors can be accepted as the evidence of the longitudinal plasma mode. However, the zero energy gap at $k=0$, does not obey to the Goldstone theorem. Therefore, an additional mechanism, which is known as Higgs mechanism, has been suggested to obtain the finite energy gap. In this point of view, the longitudinal plasma waves should be massive since Higgs bosons have finite mass [9].

As is known that, all the electroweak force particles namely weak gauge bosons ($W^\pm$ and $Z^0$ bosons) are massless in the electroweak symmetry. On the other hand, the breaking of chiral symmetry hides the electroweak symmetry (or electroweak symmetry breaking) and gives mass to the electroweak force particles $W^\pm$ and $Z^0$, leaving the photon massless. Furthermore, the electroweak symmetry breaking phenomenon determines the weak interaction limits [50]. According to Veltzmann, if the space is filled with a type of superconductor it gives mass to $W^\pm$ and $Z^0$ bosons (Goldstone bosons). This superconductor can be considered as consisting of Higgs bosons [51]. It has been proposed that Higgs boson has zero spin and angular momentum.

In this respect, we predicted that, the time reversal symmetry breaking at PME temperature, in which the angular momentum is zero, can be considered as the emerging of Higgs boson in the superconducting state. Furthermore, it has been proposed that $T_{PME}$ temperature indicates the emergence of $W^\pm$ and $Z^0$ bosons with nonzero mass. In addition, the superconducting system can be considered consisting of Higgs particles at and below $T_{PME}$. 
7. Conclusions

In this study, $T_c$ and $T_{PME}$ temperatures have been considered as the critical quantum chaotic transition points for the mercury cuprate superconducting material investigated. Both temperatures represent the transition from one state of being to another. Whereas the critical temperature, $T_c$, refers to the second order phase transition in the system, the temperature $T_{PME}$ refers to the changes in directions of the orbital currents. Furthermore, $T_{PME}$ temperature has been interpreted as the electroweak symmetry breaking point in the mercury cuprate superconducting system. These temperatures have been deduced from the experimental magnetic moment versus temperature data. Owing to the very sensitive experimental measurement system, namely SQUID, it has been proposed that the order parameter of the superconducting state hasn’t been affected or collapsed during the measurement. Therefore, magnetic measurements with SQUID can be considered as the most reliable method to obtain the most trustable information about the order parameter of the superconducting system.

As a result, this study may give an insight into the concept of cosmic DNA by means of topological solitons namely, “Segâh Solitons”, in the coherent material media and that of quantum communicating systems. Furthermore, this study may give a clue to a fundamental question of “How the electroweak symmetry is broken?” in both particle physics and cosmology.

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References

Mercury based high temperature superconductors