The Chaotic Points and XRD Analysis of Hg-Based Superconductors

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Abstract. In this article, high $T_c$ mercury based cuprate superconductors with different oxygen doping rates have been examined by means of magnetic susceptibility (magnetization) versus temperature data and X-ray diffraction pattern analysis. The under, optimally and over oxygen doping procedures have been defined from the magnetic susceptibility versus temperature data of the superconducting sample by extracting the Meissner critical transition temperature, $T_c$, and the paramagnetic Meissner temperature, $T_PME$, so called as the critical quantum chaos points. Moreover, the optimally oxygen doped samples have been investigated under both a.c. and d.c. magnetic fields. The related a.c. data for virgin(uncut) and cut samples with optimal doping have been obtained under a.c. magnetic field of 1 Gauss. For the cut sample with the rectangular shape, the chaotic points have been found to occur at 122 and 140 K, respectively. The Meissner critical temperature of 140 K is the new world record for the high temperature oxide superconductors under normal atmospheric pressure. Moreover, the crystallographic lattice parameters of superconducting samples have a crucial importance in calculating Josephson penetration depth determined by the XRD patterns. From the XRD data obtained for under and optimally doped samples, the crystal symmetries have been found in tetragonal structure.

1. Introduction

It is well known that, the superconducting materials have a phase transition from normal state to superconducting state at the Meissner transition temperature, $T_c$. The most common property of the superconductivity is the diamagnetic response to the applied magnetic field. In addition to diamagnetic response, some superconductors exhibit a simultaneous paramagnetic response under a weak applied magnetic field [1-3]. This paramagnetic behaviour is called as the Paramagnetic

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Meissner Effect (PME) and it can be observed within a specific temperature interval with the maximum value at the paramagnetic Meissner temperature, $T_{\text{PME}}$. At this temperature, the direction of the orbital current changes in the momentum space. Since both temperatures represent the transition from one to another state of being, $T_c$ and $T_{\text{PME}}$ are considered as the critical quantum chaos points of the superconducting sample [4]. The superconducting system, which is a system with two interacting electrons called as Cooper pairs, is considered to be the best material media displaying the chaotic behaviour [5-7]. In this study, the concept of quantum chaos has been discussed in the context of some critical temperatures defined at the superconducting state.

The investigated mercury based copper oxide layered superconductor, which is one of the high temperature superconductors, has the highest critical parameters such as Meissner transition temperature, $T_c$, critical current density, $J_c$, etc. The primitive cell of the mercury cuprate superconductors given in figure 1 has three superconducting copper oxide planes separated by insulating layers and this structure is considered as an intrinsic Josephson junction array. As is known, the superconductivity occurs in the copper oxide planes which form intrinsic structural layers. The origin of the superconductivity is based on the harmony which is extended to all copper oxide layers along the $c$-axis via coupling at the Josephson plasma frequency, $\omega_p$ [8].

![Figure 1. The primitive cell of Hg-1223 superconductor.](image)

Due to the highest critical parameters of the bulk superconducting HgBa$_2$Ca$_2$Cu$_3$O$_{8+x}$ (Hg-1223) samples, the determination of some electrodynamics parameters such as Josephson penetration depth, plasma frequency and the anisotropy factor has a great importance for both theoretical and various advanced technological applications. To calculate these electrodynamics parameters, the average spacing of copper oxide bilayers, $s$, is required to be measured. In this work, the bulk superconducting Hg-1223 samples have been examined by means of critical quantum chaotic points and X-ray diffraction (XRD) patterns. The critical chaotic points $T_c$ and $T_{\text{PME}}$ have been observed on both a.c. and d.c. magnetic susceptibility versus temperature data of mercury based superconductors [9].

2. Theoretical
The concept of the chaos can be defined as the transition from one state to another state where the probability density of the system, which is sensitive to the initial conditions [10], changes via temperature. In this point of view, the superconducting system is one of the best samples to understand the unexpected chaotic transitions. Superconducting systems, which exhibit the second
order phase transition, possess some critical chaos points as defined above. According to Evangelou, the phenomenon of the critical quantum chaos is observed in the quasi periodic systems, the systems with two interacting electrons and the fractal matrices [5]. Furthermore, the superconductors investigated, in which phonon mediated attractive electron-electron interaction leads to form quasiparticles, namely Cooper pairs[11-14], constitute a natural laboratory for searching and observing quantum critical chaos points [4].

The crystal structure of the mercury based copper oxide layered high temperature superconductor is used to determine the electrodynamics parameters and can be obtained from the XRD data. The average spacing of the adjacent copper oxide layers, \( s \), which is obtained from the c-axis value of the primitive cell given by the XRD data, is a crucial parameter to calculate Josephson penetration depth, \( \lambda_j \). Josephson penetration depth is inversely proportional to the square root of \( s \) value of the sample investigated [15-18].

From the view of the point group symmetry (crystal symmetry), the crystal structure of cuprates can be divided into two categories; tetragonal and orthorhombic lattices. 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 \( \text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{6+x} \) (Hg-1223) have the tetragonal crystal structure [19-21]. Since the crystal structure of the superconducting sample affects the critical quantum chaos points of the superconducting samples, the determination of lattice parameters is a necessary step to make an analogy between crystal structure and quantum chaotic points.

3. Experimental

In this work, the high \( T_c \) mercury based cuprates with different oxygen doping rates have been investigated by means of magnetic susceptibility versus temperature data and X-ray diffraction pattern analysis.

3.1. The Analysis of Temperature Dependence of Magnetization

In this study, the under, optimally and over oxygen doping procedures have been investigated by referring to \( T_c \) and \( T_{PME} \) temperatures extracted from the magnetic susceptibility versus temperature data taken by Quantum Design SQUID susceptometer model MPMS-5S. In all of the magnetization measurements, the magnetic field has been applied to the superconducting specimen along the c-axis.

The under [22], optimally [9] and over-oxygen doped [23] samples, which are very durable superconductors obtained by pressing under 1 ton weight [24]. The virgin samples have been cut by diamond saw in the rectangular shape of 4x2x1 mm. Over-doped samples have been obtained by the oxygen annealing procedure that has been performed in a furnace kept at 250°C for five hours and repeated several times [9,23].

In this article, Hg based superconducting samples have been investigated under both a.c. and d.c. magnetic fields [9,23]. The magnetic moment versus temperature data of the non-oxygen doped (as prepared) superconducting sample and the optimally doped sample obtained from the same batch have been given in figure 2 [25].
Figure 2. Magnetic moment versus temperature curves of the non-doped and optimally oxygen doped samples under a.c. magnetic field of 1 Gauss.

The related a.c. data for optimally doped virgin (uncut) and cut samples have been given in figure 3. Both data have been taken under a.c. magnetic field of 1Gauss with 1 kHz frequency.

Figure 3. Magnetic moment versus temperature curves of the virgin (uncut) and cut samples under a.c. magnetic field of 1 Gauss.
As seen in figure 3, the paramagnetic Meissner and the critical Meissner chaotic temperatures of uncut samples have been determined as 126 and 137 K, respectively. For cut sample with rectangular shape, $T_{PME}$ and $T_c$ have been found as 122 and 140 K, respectively. To our knowledge, the Meissner critical temperature of 140 K is the new world record of the high temperature superconductors under normal atmospheric pressure.

In a previous study, both $T_c$ and $T_{PME}$ of the optimally doped cut sample have been determined as 137.7 K under zero field and 1 Gauss of d.c. magnetic field [9]. The chaotic points of the under and optimally doped samples have been observed from magnetic moment versus temperature graphic given in figure 4.

![Figure 4](image)

**Figure 4.** Magnetic moment versus temperature curves of under and optimally doped samples under d.c. magnetic field between zero and 10 Gauss.

In magnetic moment versus temperature curve of cut sample taken under zero and 1 Gauss of d.c. magnetic field, the paramagnetic Meissner effect has been observed under field cooled.

### 3.2. X-Ray Diffraction (XRD) Pattern Analysis and the Lattice Parameters

The XRD pattern, from which the lattice parameters of the sample have been calculated, has been obtained from a Rigaku Model XRD device. The average spacing of copper oxide bilayers, “s”, by which the Josephson penetration depth values has been calculated, has been determined by means of the translation vectors of the mercury cuprate superconductor samples. The XRD patterns of the optimally doped and under-doped samples have been shown in figure 5 and figure 6, respectively. The lattice parameters for them have been given in table 1 and table 2, respectively [22].
Figure 5. XRD Pattern and $(hkl)$ planes (Miller indices) of optimally doped sample in 50 minutes counting. * indicates Hg-1212 and ▼ indicates Hg-1223, respectively.

Figure 6. XRD Pattern and $(hkl)$ planes (Miller indices) of under-doped sample in 7 hours counting. * indicates Hg-1212 and ▼ indicates Hg-1223, respectively.
Table 1. The lattice parameters of optimally doped sample calculated from the XRD data given in figure 5.

|          | \(a\)-axis | \(b\)-axis | \(c\)-axis  |
|----------|-------------|-------------|-------------|
|          | 3.8684 Å    | 3.8684 Å    | 15.7182 Å   |

Table 2. The lattice parameters of under-doped sample calculated from the XRD data given in figure 6.

|          | \(a\)-axis | \(b\)-axis | \(c\)-axis  |
|----------|-------------|-------------|-------------|
|          | 3.8328 Å    | 3.8328 Å    | 15.7452 Å   |

The average spacing of the mercury based sample, "s", has been derived from the \(c\) parameter of the sample. The average spacing values of the optimally and the under-doped samples have been calculated as 7.8591 Å and 7.8726 Å, respectively. Both of the average spacing values have been used to determine the Josephson penetration depth of the superconductors.

The existence of the intrinsic Josephson Effect in unconventional superconductors has indicated that these materials are natural superlattices of Josephson junctions formed on the atomic structure. The spatial period of the superlattices is only 15 Å, so Josephson junctions are densely packed in the intrinsic structure [26]. In this point of view, the mercury based copper oxide layered superconductors include a natural superlattice due to the magnitude of the translation vector which is about 15 Å.

4. Results and Discussion

Since the charge carriers of the most high temperature copper oxide superconductors are the electron holes (hole), there is a strong correlation between the hole concentration and the Meissner critical temperature. The density of the charge carriers in the superconducting sample can be increased by the procedure of oxygen annealing. In other words, optimally oxygen doping procedure results in the coupling of the uncoupled electrons in the hole type of conductivity. Therefore, over oxygen process to the superconducting sample causes extra electron doping to the system which results in some anti-symmetric contamination of the symmetric state [27].

In this study, X-ray data taken on optimally and under-doped samples have been clearly shown a mixed phase of \(\text{HgBa}_2\text{Ca}_x\text{Cu}_2\text{O}_{6+x}\) (Hg-1212) and Hg-1223. According to the data taken on both samples, the crystal symmetries have been found to be tetragonal structure with a space group of \(\text{P}4/\text{mmm}\). It has been determined that the superconducting plane (\(ab\)-plane) of the optimally doped sample is larger than that of the under-doped sample. However, the lattice parameter along the \(c\)-axis of the optimally doped sample is 0.027 Å shorter than the other one. Recalling the fact that the reduction in \(c\)-axis parameter increases the quantum tunnelling probability, so that the \(T_c\) of the optimally doped sample is higher than that of the under-doped sample. It has been first reported in this article that the optimally oxygen doped cut sample has the highest \(T_c\) of 140 K ever obtained among the superconducting samples prepared under normal atmospheric pressure. Furthermore, an
appropriate oxygen annealing has been 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 mercury based samples which have been kept in air for several months after being synthesized [28].

According to our experimental studies, it has been determined that deficiency of oxygen doping reduces the $T_c$ by about 20 K for bulk mercury based sample. Also, it has been observed that the critical quantum chaos points of the optimally doped sample are higher than that of non-doped samples. As is known, the geometric shape of the superconducting sample affects $T_c$ and $T_{PME}$. While $T_{PME}$ of virgin sample is higher than that of cut sample, $T_c$ of virgin sample is lower than that of cut sample.

5. Conclusions
In this study, the investigation of the variation of the tunnelling probability in high temperature superconductors depending on oxygen content and geometry of the sample have been realized. It is also shown that this work displays a correlation between XRD data and quantum chaos points of the superconducting sample as an indication of a bridge between the momentum and Cartesian spaces.

The determination of chaotic points has a crucial importance for technological applications of the superconductors. Hence, the prediction of chaotic points of a superconducting system enables the technologists to figure out the reliable working temperature interval for construction of superconducting devices.

6. References
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