Anomalous behavior of linear resistivity in the vanishing process along the intergrain ordering of weak-sintered ceramic superconductor YBa$_2$Cu$_4$O$_8$

M Hagiwara$^1$, A Fujii$^1$, T Shima$^2$, H Deguchi$^3$, T Shoho$^3$ and K Koyama$^4$

1 Faculty of Engineering Design, Kyoto Institute of Technology, Kyoto, 606-8585, Japan

2 Advanced Technology Center, Kyoto Institute of Technology, Kyoto, 606-8585, Japan

3 Faculty of Engineering, Kyushu Institute of Technology, Kitakyushu 804-8550, Japan

4 Institute of Socio-Arts and Sciences, The University of Tokushima, Tokushima 770-8502, Japan

E-mail: hag@kit.ac.jp

Abstract. Intergain ordering nature of weak-sintered ceramic of YBa$_2$Cu$_4$O$_8$ (Y124) is studied experimentally by ultra precise electric resistivity observation together with magnetic measurements for linear and nonlinear susceptibilities. For this purpose, a new method to detect pure linear resistivity down to the order of 1 nΩm has been developed with the help of combination technique of pulse delta method and FFT treatment. Making use of this experimental system for several weak-sintered Y124 samples, it has been revealed that linear resistivity first drops toward zero steeply with decreasing temperature, and then turns abruptly upward to forms faint maximum at lower temperature. Such peaking of electric resistivity has been found to occur below the intergrain ordering temperature that was estimated by the magnetic behavior. This newfound phenomenon, to say ‘revival of resistivity’, is being regarded as general nature for the weak-sintered ceramics, and considered to be an intrinsic frustration effect for actual d-wave type ceramics of irregular network structure.

1. Introduction

In sintered materials as aggregates of fine size grains of cuprate high-$T_c$ superconductor, of which the pairing symmetry is d-wave kind, frustration effect against the intergrain ordering is expected, because $\pi$-junctions as well as ordinary ones are necessarily included in the intergrain Josephson-coupling network.[1-5] This effect may restrain the grain system form becoming simply unified superconductive state, and thus some novel characteristics is expected in the ordering and the ordered state. On the theoretical viewpoint, a deeply studied ordering mechanism is ‘chiral glass transition’ that is random freezing of spontaneous loop-supercurrents at local intergrain circuits.[4,5]
As experimental approaches, ceramic material of stoichiometric cuprate superconductor YBa$_2$Cu$_4$O$_8$ (Y124) has been studied continuously by the authors, and the following facts were reported. Through the magnetic measurements, two-step-wise dc magnetization behavior against temperature clearly reflects the transition process from intragrain to intergrain orderings,[6] and a singular peak of nonlinear magnetic susceptibility is formed at the intergrain ordering temperature $T_{c2}$.[7] Besides, through the measurements of the electric ac resistivity, tailing of linear resistivity was detected around temperature region below $T_{c2}$, and it was discussed to be a possible frustration effect of the intergrain ordering.[8] Afterward recently, nonlinear magnetic susceptibility of the Y124 samples prepared by various sintering conditions were studied, and it has been found that another anomaly may appear apart from the chief negative singular peak at $T_{c2}$ when the sintering duration is not so long.[9] This result has suggested that the intergrain ordering process advances with some inhomogeneous nature,[10] and that successive change in the ordering structure might be caused. If that is the case, the successive behavior is thought to be reflected naturally by electric transport phenomena for the samples of the frustrated ceramic superconductor.

Thus the present subject is directed to clarify detailed behavior of linear resistivity in the process of intergrain ordering for the weak-sintered ceramic Y124. Here we should note that possible resistivity brought by the fluctuation in the ordered state holding frustration must be reflected by linear resistivity, yet the signal revel is estimated to be order of n\(\Omega\)m or less.[5] In order to examine such intrinsically small resistivity, therefore, a new experimental method of enough performance in both sensitivity and offset elimination is now required. Accordingly, the authors designed and constructed a new measurement system for linear and nonlinear resistivity observation, using combination techniques of ‘delta method’ [11] by pulse applied current and Fourier analysis method for the periodic measurements by sinusoidally sequenced excitation current pulses. With this system, intrinsic temperature dependent behavior of very weak but physically valid signal of linear resistivity is searched near and below $T_{c2}$ for several samples of the weak-sintered ceramic Y124.

2. Experimental

First of all, fine-powder form Y124 was obtained as the calcined product of the developed synthetic method.[12,13] Then, the calcined powder was sieved by mesh size down to 10\(\mu\)m, and then was press-molded into pellets using pressure in range of 9.3-18.5 MPa. These obtained several pellets were sintered at 780°C for 25-50 h, to be the weak-sintered ceramic series with varied forming and sintering conditions.

Our new measurement system for very weak electric resistance is outlined as follows. Elemental working is 4-wire voltage-drop detection by ‘pulse-delta-method’ that can compensate time-dependent offset signal using three excitation current pulses alternating quickly between a set value and zero. As the further advanced method (named SSPD), the current pulse height $I(n)$ is sequentially swept along sinusoidal waves as $I(n)=I_0\sin(2\pi n/512)$ (with $n=0-511$), and the stationary response of the voltage drop $V(n)$ for each step is measured and stored. The unit periodic measurement of 512 points is repeated optionally settled times, and the accumulated multi periods data are averaged into one periodic data in order to increase the S/N ratio or the final sensitivity.

Such obtained periodic voltage data are analyzed by FFT to be decomposed into fundamental and harmonic components with a computer. The derived in-phase $n$-th harmonics is represented by $V'_{n\omega}$ and the quantity $V'_{1\omega}/I_0$ correspond to first term approximation for linear resistance as the first expansion coefficient of $V(I)$. It is noted that the analyzed data cannot inform us of any physically dynamic characteristics, because each unit pulse measurement is executed at stationary state.

Using this SSPD method with current $I_0=8$ mA, precise resistivity behaviors for the several prepared ceramic samples are traced against temperature. At each controlled temperature, the periodic sweep was repeated 4 - 16 times, which was changed with the signal level. The resistivity results in this report are chiefly shown in quantity $\rho_{1\omega}$ as the first-term-approximated linear resistivity that was reduced by taking into account the sample size factor.
Figure 1. Full range temperature variation of linear resistivity for weak-sintered ceramic of YBa$_2$Cu$_4$O$_8$. The main view results were measured by SSPD (see the text) method by excitation pulse height of 8 mA, and the values were shown by fundamental resistivity $\rho_{1\omega}$. The results of the insert were measured by ordinary delta-method of excitation current 4 mA.

Figure 2. Perpendicularly enlarged scopes of the linear resistivity, by re-plotting the same data in the main view of Figure 1. Applied magnification is 50 for (a) and 4200 for (b).

For one of the typical samples, magnetic behaviors were also observed by a SQUID system. AC susceptibilities $\chi'$ and $\chi''$, and harmonic magnetizations $M_{\omega}$ were measured with weak excitation magnetic field of frequency 1.0 Hz and amplitude of 0.1 Oe, and then the temperature dependences were examined in comparison with the electric resistivity data.

3. Results and discussion
In the present report, we primarily focus on a sample, that was obtained by 50h sintering, among the several prepared weak-sintered ceramic samples. The experimental result will show a new novel behavior of linear resistivity just below the intergrain ordering temperature $T_{c2}$. To begin with, the full range behavior of $\rho_{1\omega}(T)$ is shown in Figure 1. The characteristic dropping curve of resistivity certainly reflects typical temperature dependence of ceramic Y124 showing the intergrain ordering.[8] To describe from higher temperature side, $\rho_{1\omega}$ begins steep dropping around 81 K (i.e. $T_{c1}$ of crystalline Y124), then gradually lowers during intergrain incoherently disordered state, and finally tends to (almost) zero toward intergrain ordering state. Possible minute resistivity near and below this ordering temperature is a matter of the present concern.

Now, the data around the critical region in Figure 1 are re-plotted in two-stepwise expanded views of Figure 2 (a) and (b), whose respective longitudinal scopes are 1/50 and ~1/4200 of the full area. Seeing in comparison the temperature regions where $\rho_{1\omega}$ appears to reach zero in Figures 1 and 2, we notice that the $\rho_{1\omega}(T)$ curve remains non-zero tailing in the more expanded views. When the scope becomes of Figure 2 (b), instead of such apparent lowering of the vanishing temperature, an unexpected anomalous curve appears at the lower temperatures. To show precisely, further enlarged view is drawn in Figure 3 with the help of moving-average-filtering. Seen from high temperature side in this figure, while $\rho_{1\omega}$ first approaches zero monotonously, the dropping abruptly changes to rising at ~52.6 K, forming a minimum just the above zero level. Below this temperature, $\rho_{1\omega}(T)$ shapes a
somewhat broad peak around \( \sim 46 \) K, and then it decreases again with the lowering temperature. Such found behavior of \( \rho_{\text{rev}} \) 'revival of resistivity' as it were, is a very novel phenomenon as against ordinary resistivity change for superconductive transitions.

Here we take the magnetic behaviors into consideration. First, in-phase linear component of ac magnetic susceptibility, \( \chi' \), and out-of-phase one, \( \chi'' \), are shown together in Figure 4. The curve of \( \chi'(T) \) qualitatively traces typical temperature variation of zero-field-cooled dc magnetization whose absolute value shows drastic rising from intragrain Meissner signal to full shielding signal owing to the intergrain-ordering phenomenon.[6] As for the behavior of \( \chi''(T) \), the positive peak indicates initial-phase-lead effects around the ordering process. These behaviors confirm that this ceramic is a typical sample of the present subject of the intergrain ordering. Next, nonlinear magnetic susceptibility \( \chi_2 \) is examined in order to clarify the critical temperature of this ordering. Using the previously reported method by the authors',[14] temperature variation of \( \chi_2 \) is estimated from series summation of the measured harmonic magnetizations of \( M_{n\omega} \) with \( n=3, 5, 7 \), and the result is revealed as shown in Figure 5. A conspicuous negative peak with singular feature is formed at around 55 K. This behavior is a reflection of cooperative phase transition, and the peak position informs precisely that the critical point \( T_{c2} \) is \( \sim 54.5 \) K. Now this temperature position is marked with the vertical line on the already presented Figure 3. It has been then clarified that the found ‘revival phenomenon’ of linear electric resistivity is certainly an occurrence below \( T_{c2} \) that is decided as the singular point of magnetic nonlinear susceptibility.

The experimentally observed signal of the ‘revival phenomenon’ seen in Figure 3 is no larger than the order of 1 nV level that may be easily affected by various drift-error origins, so that we should confirm reproducibility and generality for the phenomenon. For this purpose, it is noted first that the \( \rho_{\text{rev}}(T) \) feature was well reproduced by several repeated temperature sweeps near the revival peak region, and actually, several plotted points around 45 K in Figure 3 were such repeat-checked data. Next, the generality can be speculated as follows. In the early stage of this study, it was varied with the samples that the ‘revival’ behavior was observed or not. However, it is being known that more sensitive measurement, that is attained by increasing of the accumulation times of the voltage data, often reveals the weak ‘revival’-like phenomenon, though the S/N condition is severe. One of such cases has resulted for the ceramic sample prepared by 25 h sintering, and the revealed behavior of \( \rho_{\text{rev}}(T) \) is illustrated in Figure 6, in which the extremely enlarged view was obtained through both 16-periods accumulation for each measurement point and post filtering by moving-average. Though the data points are fluctuating, we can recognize the ‘revival phenomenon’ in this figure. To observe the
behavior from higher temperature side, \( \rho_{1\omega} \) first drops monotonously with decreasing temperature down to \( \sim 55 \) K, and once attains almost zero around 40-45 K, and then looks to turn upward and to form a maximum at around 30 K. The restored resistivity from zero is a purer ‘revival’ as it were. It has been also noticed for the other weak-sintered samples, such a revival-like phenomenon can be often observed, though each signal level and peak position are diverse for the samples. Accordingly, it is rather natural to regard the revival of resistivity as a quantitatively general phenomenon inherent in our weak-sintered ceramic samples. In this understanding, impurity effects or other extrinsic sample problems may be eliminated, because temperature position of the ‘revival’ peak changes correlating with \( T_c \) for each sample.

Our interest is now taken in possible origins of the revival phenomenon. Whereas decisive discussion cannot be done at present, a clue to the understanding is noticed to consist in structural inhomogeneity of the ordering process. For a theoretical model of frustrated gain network on regular lattice system, non-zero linear resistivity has been suggested to remain at the ordered state.[6] Differently, the ceramic systems in the present study are formed as assembly of actual grain particles and include various irregularity or inhomogeneity. In such irregular systems, the intergrain short-range ordering might progress in mesoscopically inhomogeneous manner. As a possibility, it is considered that intergrain (ordinary-type) superconductive ordering of dispersed non-frustrated regions is advanced ahead the whole ordering including frustration. If such like mixed ordering structure is realized, it seems rather natural that the resistivity first drops toward zero steeply, because lower resistivity region must rule whole resistivity through shunting effects of many conductive passes, in the structurally mixed systems. However, on the other hand, frustration origin certainly exist in the ceramic will exert final ordered state, because cooperative ordering as a whole system must require reconstruction of the incompletely ordered state. We consider that the observed ‘revival phenomenon’ of resistivity is an essential and detectable reflection by the frustration in such irregular ceramic systems.

A problem to be studied is in the relation between the resistivity phenomenon and the magnetic behavior. The speculated reconstruction of the ordered structure must be nothing but a kind of phase transition. So, it is naturally considered that the magnetic responses, including linear and nonlinear

---

**Figure 4.** Temperature dependences of linear magnetic susceptibilities \( \chi' \) and \( \chi'' \) measured by excitation field of frequency of 1.0 Hz and amplitude of \( h=0.1 \) Oe, for the same ceramic sample of YBa\(_2\)Cu\(_4\)O\(_8\) as shown in Figures 1-3. The insert shows enlarged view around the rising region of \( \chi' \) and \( -\chi'' \).

**Figure 5.** Temperature dependence of nonlinear magnetic susceptibility \( \chi_2 \) estimated from series summation of harmonic magnetizations \( M'_{\omega n} (n=3, 5, 7) \) obtained together with the data in Figure 4. The applied series formula is shown in the figure.
terms, may form some anomaly at around 45 K in Figures 1-5 for the main sample in this report. While such an indication may be found in $\chi(T)$ of Figure 5, the linear susceptibilities do not show any apparent anomaly in Figure 4. However, besides, the authors has preliminarily observed that some samples show detectable anomalies of $\chi'$ and $\chi''$ as well as the nonlinear magnetic responses. Comprehensive experiments for both magnetic and resistive observations using the authors’ latest method are progressing, in order to discuss more decisively and reveal the ordering nature affected by frustration in actual ceramic superconductor systems.

**Acknowledgment**
The authors express finally that this work was supported by both Grant-in-Aid for Exploratory Research (40655001) and Grant-in-Aid for Scientific Research on Priority Areas (19052006).

**References**

[1] Kusmartsev F.V *Phys. Rev. Lett.* **74**, 2268
[2] Sigrist M, Rice T.M *Rev. Mod. Phys.* **67**, 503
[3] Choi M.Y and Stroud D, *Phys. Rev.* **B 35**, 7109, and the references therein
[4] Kawamura H, *J. Phys. Soc. Jpn.* **64**, 711, Kawamura H and Suan Li *M Phys. Rev. B* **54**, 619, Kawamura H and Suan Li M *J. Phys. Soc. Jpn.* **66**, 2110
[5] Kawamura H *J. Phys. Soc. Jpn.* **69**, 281
[6] Kawachi M, Hagiwara M, Koyama K and Matsuura M *J. Phys. Soc. Jpn.* **63**, 3405
[7] Matsuura M, Kawachi M, Miyoshi K, Hagiwara M and Koyama K *J. Phys. Soc. Jpn.* **64**, 4540
[8] Yamao T, Hagiwara M, Koyama K and Matsuura M *J. Phys. Soc. Jpn.* **68**, 871
[9] Hagiwara M, Yamao T, Shima T, Deguchi H and Matsuura M *Physica C* 412-414, 94
[10] Hagiwara M, Shima T, Kitada R, Deguchi H and Koyama K *Physica C* **470**, 1052
[11] Daire A *Online article titled as ‘Low-Voltage Measurement Techniques’*
http://www.evaluationengineering.com/archives/ArchiveWrapper.aspx?file=0605/0605low_voltag.asp
[12] Koyama K, Junod A, Graf T, Triscone and G and Muller J *Physica C* **185-189**, 461
[13] Hagiwara M, Yamao T and Matsuura M *Physica C* **392-396**, 66
[14] Hagiwara M, Shima T, Yamao T, Deguchi H and Matsuura M *Physica E* **29**, 534