STUDY OF SUPERCONDUCTING PROPERTIES OF OXYGEN DEFICIENT $\text{GdBa}_2\text{Cu}_3\text{O}_{7-y}$ BY A HEATING CYCLE TECHNIQUE

H.E. HORNG, J.C. JAO * and M.H. HSIEH **

Department of Physics, National Taiwan Normal University, Taipei, Taiwan

H.C. YANG, B.C. YAO and C.H. CHEN

Department of Physics, National Taiwan University, Taipei, Taiwan

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We have studied oxygen deficient $\text{GdBa}_2\text{Cu}_3\text{O}_{7-y}$ samples by a heating cycle technique and correlated the resistivity data with the oxygen deficiency derived from TGA. An orthorhombic to tetragonal phase transformation was found at about 720 K and it is consistent with that derived from the X-ray data. The resistivity is hysteretic cooling and shows semiconducting behavior for $y \geq 0.7$. Localization was found for samples with semiconductive properties. The electron–phonon coupling constant derived from the electric and magnetic measurements is $\lambda_{tr} = 0.31$ which suggests a weak electron–phonon coupling in high- T_c oxides.

The electric properties of the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ depend strongly on the oxygen content. The X-ray and neutron diffraction method have made it clear that the high T_c is an orthorhombic phase and that the oxygen around 7.0 gives the best superconducting properties. As the oxygen content is decreased, the material will enter the tetragonal phase, and superconductivity is destroyed. Very recently the role of oxygen on superconductivity has been examined on $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ by several researchers [1–8]. Some works [9,10] show that $\text{GdBa}_2\text{Cu}_3\text{O}_{7-y}$ exhibits the same superconducting and structure characteristics as that of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$.

In this work we present a systematic study of superconducting properties of oxygen-deficient $\text{GdBa}_2\text{Cu}_3\text{O}_{7-y}$ by a heating cycle technique. In technique we heated the sample to various high temperatures to desorb oxygen out of the sample and measured the resistivity in a cycle. We calculate the

corresponding $7-y$ values according to the formula:

$$W\% = \frac{(\text{weight of GdBa}_2\text{Cu}_3) + 15.996(7-y)}{\text{weight of GdBa}_2\text{Cu}_3\text{O}_{7-y}} \quad (1)$$

where $W\%$ is the TGA result (Du Pont 9900) which is performed under the same conditions as that of the resistivity measurement. In eq. (1) it is assumed that the weight losses are due to oxygen only. The results obtained from eq. (1) were our calibration standard in determining the oxygen content for $\text{GdBa}_2\text{Cu}_3\text{O}_{7-y}$ at high temperatures (inset of fig. 6). We believe the heating cycle will provide us a new approach of studying transport properties of oxygen-deficient samples.

The samples used in this study were prepared by mixing BaCO_3 , Gd_2O_3 and CuO , grinding, and heating at 950°C in air for 1 day. These materials were then pressed into pellets, sintered in flowing oxygen at a temperature of 950°C for 16 hours, 700°C for 12 hours and slowly cooled to room temperature. The powder X-ray data show that the obtained sample was nearly single phase. The shape of the sample was a rectangular bar with a cross section of about 4 mm^2 . The resistivity was measured by an AC four-probe

* Present address: National Defense Medical Center, Taipei, Taiwan.

** Present address: Provincial Chia-Yi Teachers College, Chia-Yi, Taiwan.

method. For Pt wires were connected to the sample by mechanical pressure in the high temperature range ($T > 300$ K) and by silver paint in the low temperature range ($T < 300$ K). The resistivity was measured in helium atmosphere. Several samples were studied in this work. Data reported here were typical results.

Data characterizing the room temperature resistivity after the heating cycle are shown in table I. The y values are derived from TGA data. ρ_a (300 K) is the resistivity of sample a at room temperature which is about $2.2 \text{ m}\Omega \text{ cm}$. The resistivity ratio relative to sample a at room temperature increases monotonously as one decreases the oxygen content. Figures 1 and 2 show the temperature dependence of the electrical resistivity for $\text{GdBa}_2\text{Cu}_3\text{O}_{7-y}$ samples up to several high temperatures in a complete cycle. The resistivity is normalized to its room temperature value ρ (300 K). A few interesting features are worth noting. First, the resistivity is hysteretic in cooling. Secondly, the resistivity changes gradually from the metallic to semiconducting behavior as one increases the oxygen deficiency. Finally, a linear temperature dependence was found in the cooling curve for sample b as shown in fig. 1(a). In this cooling curve sample b shows metallic behavior.

Figure 3 shows the temperature dependence of ρ for the $\text{GdBa}_2\text{Cu}_3\text{O}_7$ sample at $T > 300$ K. One can see that in the high temperature regime ($T > 400$ K), the order to disorder transformation causes the electrical resistivity to departure its linear behavior and

Table I

Data characterizing the electrical properties of the samples. The oxygen content is derived from TGA data. The ρ (300 K)/ ρ_a (300 K) is the resistivity ratio relative to sample a at room temperature.

Samples	Oxygen content ($7-y$)	ρ (300 K) / ρ_a (300 K)	T_c (50%) (K)
a	7	1	92.9
b	6.79	1.14	91.6
c	6.71	1.18	88.6
d	6.59	2.68	83.5
e	6.50	4.65	81.8
f	6.45	4.73	50.0
g	6.41	8.74	37.0
h	6.29	141.6	-
i	6.16	239.1	-
j	6.10	715.0	-

Fig. 1. (a) Relative resistivity versus T for sample b and e. (b) Relative resistivity versus T for sample f and g. The arrow indicates the direction along which the electrical resistivity is measured.

Fig. 2. Temperature dependence of ρ for samples h, i, and j.

an orthorhombic to tetragonal phase transformation was found to occur at 720 K as shown in the inset of fig. 3. This high temperature electrical resistivity is similar to that of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ samples [5]. The orthorhombic to tetragonal phase transformation was further checked by the powder X-ray data. Figure 4

Fig. 3. Temperature dependence of ρ for sample $\text{GdBa}_2\text{Cu}_3\text{O}_7$. $d\rho/dT$ as a function of T is shown in the inset.

Fig. 4. Variation of lattice parameters with the highest heating temperatures.

shows the room temperature lattice parameters of the samples derived from the powder X-ray data. We noted that the temperatures reported here referred to the highest heating temperatures used in the resistivity measurement. The orthorhombic to tetragonal phase transformation was found to occur at about 750 K which is a bit higher than that obtained from the resistivity data.

Figure 5 shows T_c as a function of y 's and ρ versus T at 200 K, 290 K and 300 K for different samples. One can see that T_c decreases as one increases the value of y . There is a sharp drop in the T_c 's which occur in $6.4 < y < 6.5$. The sample with $y=0.6$ has $T_c(50\%)=37$ K and a transition width of about 26 K. The sample with $y=0.7$ is semiconducting.

It is known that the equilibration time is important in determining the transport properties of the sample. If the heating rate is too fast, it is likely that the resulting oxygen deficient samples have a non-uniform parameter y . That is the cores of the grains have a larger oxygen content and have a higher T_c which is not revealed by the resistance measurement. So the effective y is less than the sample average as determined by the thermogravimetry measurement. To see whether the problem in the uniformity of the sample is serious or not, the magnetic susceptibility, which is a probe of the bulk superconductivity, which is a probe of the bulk superconductivity,

Fig. 5. The variation of the superconducting temperature as a function of y 's, also shown is ρ versus T at 200 K, 290 K and 300 K.

tivity, is also measured. The magnetic susceptibility data show nearly the same superconducting transition temperature indicating that sample uniformity is not a serious problem. If the uniformity was a problem, the derived value of $y=0.7$ at the onset of the semiconductivity is an upper limit. That is, the real value y for the onset of the semiconductivity should be less than 0.7. Up to now there are no available data on the GdBa₂Cu₃O_{7-y} system, so a direct comparison between the results reported here and the available data is impossible. It is worth comparing the data with that of YBa₂Cu₃O_{7-y}. The y value at the onset of the semiconductivity is nearly the same as that derived from the quenched YBa₂Cu₃O_{7-y} [6] which we believe are more uniform in the oxygen-deficient stoichiometry. The results reported here and that reported in ref. [6] indicate that the sample uniformity in oxygen stoichiometry is not a serious problem for the experiments.

We have used heating cycle to desorb oxygen out of the samples. The advantages are that we can measure the electrical resistivity in a cycle that the effects of oxygen deficiency on resistivity can be mapped out clearly. This can be seen from the plot of $\rho - \rho(0) - \beta T$ versus $y/(0.6-y)$ (fig. 6) for sample f, where $\rho(0)$ is the extrapolated residual resistance, β is derived from the linear temperature dependence of ρ between $T=300$ K and 120 K, y is the oxygen deficiency obtained from the TGA data. $\rho - \rho(0) - \beta T$ is the contribution of resistivity due to oxygen deficiency. $y/(0.6-y)$ was chosen as ab-

Fig. 6. $\rho - \rho(0) - \beta T$ as a function of $y/(0.6-y)$. y versus T is shown in the inset.

scissa so that we can compare our present results with that reported in ref. [11], here we have chosen δ_c in ref. [11] to be 0.6 in our plot. The oxygen deficiency, y , as a function of temperature is shown in the inset. The disadvantage is that it may cause the non-uniformity in the oxygen-deficiency stoichiometry. Therefore one should be careful in performing the experiment to avoid those problems. That is, the experiment should be done as slowly as possible. In our experiment the heating rate is about 5°C/min.

In the semiconducting regime, we can write

$$\rho/\rho(300 \text{ K}) = Ae^{-c/k_B T}, \quad (2)$$

where c is an activation energy and A is a constant. A plot of $\ln \rho$ versus $1000/T$ is shown in fig. 7. One can see that a linear behavior of $\ln \rho$ versus $1/T$ was found and the derived activation energy is shown in the inset. The transport properties in the semiconducting region have been reported in ref. [11] for different YBa₂Cu₃O_{7-y} samples. Similar behavior in $\ln \rho$ versus $1/T$ was reported and the activation energy obtained here for GdBa₂Cu₃O_{7-y} samples is of the same order of magnitude as that reported in ref. [12] for YBa₂Cu₃O_{7-y}. Figure 8 shows the temperature dependence of $\ln \rho$ versus $(1/T)^{1/4}$ at low temperatures, a linear behavior in $\ln \rho$ versus $(1/T)^{1/4}$ was found. These data suggest that the ordered to disordered transformation in the oxygen-deficiency stoichiometry has occurred while we heat up the sample. So the transport properties of the sample be-

Fig. 7. $\ln \rho$ as a function of $1000/T$ for samples h, i, and j.

Fig. 8. $\ln \rho$ versus $1/T^{1/4}$ for samples h, i, and j.

have like that of the disordered materials [13].

It is known that normal state resistivity will provide us information about the superconducting properties of the samples. Chakraborty, Pickett and Allen [14] have shown that the phonon limited resistivity, ρ , for $T > \theta_D$ (Debye temperature) can be expressed as

$$\rho = [(n/m^*)e^2\hbar]^{-1} 2\pi k_B \lambda_{tr} T, \quad (3)$$

where n is the carrier density, λ_{tr} the electron-phonon coupling constant. If one uses the London penetration depth, $\lambda_L = [m^*/(ne^2\mu_0)]^{1/2}$, to derive n/m^* , where μ_0 is the permeability in free space puts m^*/n into eq. (3), one can obtain λ_{tr} . Using the $\lambda_L = 0.6 \mu\text{m}$ value of ref. [15], one gets $\lambda_{tr} = 0.31$. The λ_{tr} value represents moderate to weak electron-phonon coupling and would predict T_c of about 0.4 K if McMillan equation [16] was used with $\mu^* = 0.1$. We noted that there are models [17] where such values of coupling constant can lead to a high T_c if the Fermi level is near two dimensional Van Hove singularity. Of course, it is not yet known if this model is correct and it is possible one needs another mechanism.

In conclusion, the heating cycle technique has been used to characterize the transport properties of oxygen-deficient $\text{GdBa}_2\text{Cu}_3\text{O}_{7-y}$ samples. An orthorhombic to tetragonal phase transformation was found to occur at about 720 K in helium atmosphere

which is consistent with that derived from the powder X-ray data indicating that an irreversible process has occurred in the phase transformation. This is a reasonable result because the resistivity of the sample was measured under the helium atmosphere and a hysteresis curve should be found in the cooling curve. Localization was found for samples with semiconductive properties. The electron-phonon coupling constant is $\lambda_{tr} = 0.31$ which suggests that the phonon mediated electron-electron interaction is too weak to have high- T_c superconductivity and it is possible that one needs another mechanism for high- T_c oxides.

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