Impedance and heat capacity anomalies in Y–Ba–Cu–O ceramics at $T > T_c$

V M DMITRIEV, V N EROPKIN, A M GUREVICH,
M N OFITSEROV and N N PRENTSLAU

Institute for Low Temperature Physics and Engineering, UkrSSR Academy of Sciences,
Kharkov, USSR

Abstract. Peculiarities of rf and thermodynamic properties of Y–Ba–Cu–O ceramics in the normal state are detected. These include frequency oscillations of resistance in the range $\sim 10^7$ to 2×10^9 Hz, dielectrization of ceramic properties below 10^6 Hz, temperature dependence of impedance for different frequencies, intercorrelating anomalies of temperature dependences of heat capacity and ohmic resistance.

Keywords. Impedance; heat capacity; ceramics; anomaly.

1. Introduction

Earlier studies have reported the existence in yttrium ceramics of anomalies in the electromagnetic field power absorption (Shcherbakov *et al* 1987), thermal conductivity (Jezowski *et al* 1989), heat capacity (Loram *et al* 1989), as well as mechanical properties, such as internal friction (Xiaohua *et al* 1988), microplasticity (Peschanskaya *et al* 1988) and others (Morgun *et al* 1988). To elucidate their nature and correlation dependences between some of them, as well as to reveal new phenomena at 90 to 300 K, we have carried out a number of experiments on measuring the ceramics impedance in the frequency range of 10^5 to 10^{10} Hz and its heat capacity.

2. Samples and measurement technique

The $\text{YBa}_2\text{Cu}_3\text{O}_x$ samples under investigation were made in the form of a parallelepiped ($2.6 \times 4 \times 16.3$ mm, sample 1) and a cylinder (10.5 dia $\times 6.5$ mm, sample 2). The sample resistivity was $\rho \approx 10^{-4}$ ohm m at $T = 300$ K. The specific weight of samples was ≈ 3.62 g/cm³. The resistivity was measured by the four-probe method and the impedance by the resonator method. The ohmic resistance R_s was determined by the change of Q -factor, the reactive impedance component was estimated by the change of resonance frequency. Annealed copper was used as a standard and the reference material was brass.

The heat capacity C_p was measured by absolute calorimetry in the temperature range from 78 to 274 K with an accuracy of 0.3%.

3. Experimental results

3.1 Frequency oscillations of microwave field power absorption

The frequency dependence of R_s for sample 1 is shown in figure 1 at $T = 300$ K. At frequencies below 10^7 Hz the ohmic resistance can be presented as $R_s \propto f^{1.2-1.4}$ with

Figure 1. Frequency dependence of R_s at $T = 300$ K.

insignificant amplitude deviations about this value. In the frequency range from 10^7 Hz to 2×10^9 Hz the R_s anomalies take the form of frequency oscillations. In this frequency range some samples display two-frequency intervals in which the oscillations occur. Figure 1 shows the values of $R_s = F(f)$ of such sample (sample 1, curve 1). Here the oscillations are observed at intervals I and II, and are absent in interval III. Curves 2 and 3 reflect the dependences of $R_s = F(f)$ for brass and copper, respectively.

Irrespective of whether one- or two-frequency intervals of oscillations are observed in the sample, the following general regularities are typical of R_s .

There exists the range of frequencies where the oscillation amplitude varies but insignificantly (at the beginning of range II). Here $R_{s\min}$ are limited by the curve $R_s \propto f^{0.5}$ while $R_{s\max}$ are limited by the curve $R_s \propto f^{0.3-0.4}$. Note that $R_s \propto f^{0.3}$ is observed in samples where oscillations are absent (Belsky et al 1987) and $R_s \propto f^{0.5}$ is characteristic of metals.

The ratio of frequency of the following R_s maximum to the frequency of the preceding one is within 2.2 to 2.3.

$R_s = F(f)$ correlates with the penetration depth δ . This follows from the consideration of $K = F(f)$ dependence shown in the inset of the figure, which is the ratio of resonant system frequency shifts when the samples of ceramics under study and standard copper are introduced into the magnetic field. The existence of correlation between R_s and K is characteristic of metals. In the frequency range $f < 5 \times 10^6$ Hz the penetration depth increases noticeably at the abrupt decrease of losses which become even lesser than in copper and brass. The ceramic properties are dielectrized.

At frequencies above 2×10^9 Hz there are no oscillations, but R_s drops with increase of frequency and at $\sim 10^{10}$ Hz takes the values comparable to 10^8 Hz (Shcherbakov *et al* 1987). When the ceramics temperature was decreased, the frequency oscillations of R_s were observed down to T_c .

3.2 Temperature dependences of R_s and C_p in the ceramics

We have found three kinds of dependences in the same ceramic sample depending on the irradiation frequency: $R_s = F(T)$ and $dR_s/dT < 0$; $R_s \neq F(T)$ and $dR_s/dT > 0$, though at direct current $\rho = F(T)$ and $d\rho/dT > 0$.

Figure 2a shows the temperature dependence of $R = R_s(T)/R_{s(300)}$ at a frequency of 3.5×10^5 Hz (curve 1) and $r = \rho(T)/\rho_{(300)}$ (curve 2) of sample 1. It is seen here that $R(T)$ presents the semiconductor properties, while $\rho(T)$ conforms to the metallic ones. Figure 2b shows a set of curves $R_s = f(T)$ for various frequencies ($1 - 10^5$ Hz, $2 - 7.5 \times 10^5$ Hz, $3 - 80 \times 10^5$ Hz) of sample 2. The inset of this figure shows the dependence of $R_{s(92)}/R_{s(300)} = F(f)$ of sample 2. Figure 2c shows the temperature dependence of its heat capacity C_p .

Figure 2. (a) Temperature dependence of R and r in sample 1. (b) Temperature dependence of R in sample 2 at the frequencies: $1 - 10^5$ Hz, $2 - 7.5 \times 10^5$ Hz, $3 - 8 \times 10^6$ Hz. The inset shows the frequency dependence of $R_{s(92)}/R_{s(300)}$ in sample 2. (c) Temperature dependence of C_p .

It follows from figure 2b that semiconductor properties are observed up to the frequencies of about 7.5×10^5 Hz where $R_s \neq F(T)$. Above this frequency the sample displays the metallic character of R_s vs T dependence except the anomaly at $f \approx 6 \times 10^6$ Hz where $R_s \neq F(T)$ again.

3.3 Temperature anomalies of R_s and C_p of the ceramics

The intercorrelating anomalies of R_s and C_p are detected in the temperature intervals 155–170 K, 210–240 K and at ~ 270 K. These anomalies are shown in figure 3. Figure 3a relates to R_s of sample 1, figures 3b, c to R_s of sample 2, figure 3d to C_p of sample 1. It is peculiar that the polarity of R_s anomalies at $T = 210$ K and $T = 230$ K depends on whether the general $R_s(T)$ behaviour at the measurement frequencies is of semiconductor or metal type as seen from figure 3. Here the anomaly in sample 1 was measured at a frequency of 3.5×10^5 Hz. In sample 2 it was measured at 10^5 Hz (figure 3b) and 2.2×10^6 Hz (figure 3c). The anomalies of R_s and C_p are also observed at the temperatures 235–240 K. Note that the anomalies of $\rho = F(T)$ are not observed, except very small ones at $T \sim 270$ K, though some workers note their existence (Jezowski et al 1989).

Figure 3. Anomalies of R_s and C_p . Anomalies of R_s : (a) sample 1, $f = 3.5 \times 10^5$ Hz; (b) sample 2, $f = 10^5$ Hz; (c) sample 2, $f = 6 \times 10^6$ Hz; (d) anomalies of C_p in sample 1.

4. Discussion

The detected frequency oscillations of the microwave electromagnetic field power absorption by yttrium ceramics are probably due to the size effects at the ceramics inhomogeneities as is the case for samples of finite geometry (Fisher and Kao 1969). The impedance of ceramics is a composite function of frequency and temperature, apparently representing its phase and dynamics peculiarities. The dielectrization of ceramic properties at low frequencies can be caused by the fact that ceramics structure resembles that of superlattices.

The detected temperature anomalies of R_s and C_p at $T \sim 160$ K look similar to those in the region of superconducting transition. They are stable in time and during thermocycling. The magnetoresistance data (Cai and Larbalestier 1987) also speak in favour of the superconducting phase appearance at these temperatures.

According to our results, the anomalies at $T = 210$ K and 230 K are related to the phase transitions of the first order since both anomalies essentially depend on the temperature history of the sample and kinetic characteristics of the experiment, heating rate, temperature "step". Moreover, the processes causing hysteresis of the temperature dependence proceed in the temperature range 180 – 230 K. This is evidenced by lowering of the "regular" curve $C_p(T)$ if the initial temperature of a series of measurements falls within the above region. Beyond this range of temperatures, all the measurement series are reproduced to within the experimental accuracy.

5. Conclusion

Thus, we have detected the peculiarities of high-frequency and thermodynamic properties of $\text{YBa}_2\text{Cu}_3\text{O}_x$ ceramics in the normal state. These peculiarities include frequency oscillations of resistance in the frequency range 10^7 – 2×10^9 Hz, dielectrization of the ceramics properties at frequencies below 10^6 Hz, the resistance temperature behaviour and the dR_s/dT sign dependence on the frequency of measurements taken on the same samples, intercorrelating anomalies of temperature dependences of heat capacity and high-frequency ohmic resistance. The characteristic temperatures of anomalies are 160 K, 210 K, 230 K and 270 K.

Acknowledgements

The authors express their gratitude to I V Zolocheskii and E V Khristenko for measuring the d.c. resistance.

References

- Belsky M, Gaidukov M M, Golman E K, Karpyuk A, Karmanenko S F and Kozyrev A B 1987 *Problems of high-temperature superconductivity* (Sverdlovsk) 2/127
- Cai R Y and Larbalestier D C 1987 *Phys. Rev. Lett.* **58** 2788
- Fisher H and Kao Y H 1969 *Solid State Commun.* **7** 275
- Jezowski A, Klamut J and Troinar Ja 1989 *Fiz. Nizk. Temp.* **15** 1025
- Loram I W, Mirza K A, Joyce C P and Osborne A I 1989 *Europhys. Lett.* **8** 263

- Morgun V N, Sokolov A G, Popov V P, Chebotarev N N, Panfilov A S and Svechkarev I V 1988 *All-Union conference on high-temperature superconductivity* (Kharkov) vol. 3, p. 1903
- Peschanskaya N N, Shpeizman V V, Yakushev P N and Smirnov B I 1988 *All-Union conference on high-temperature superconductivity*, (Kharkov) vol. 3, p. 203
- Shcherbakov A S, Katsnelson M I, Trefilov A V, Sorokin N A, Valiulin E T and Petrov A N 1987 *Pis'ma Zh. Eksp. Teor. Fiz.* **46** 111
- Xiaohua C, Linhat S, Yening W, Huimin C and Lang Yu 1988 *Mod. Phys. Lett.* **B2** 737