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Magnetization and critical currents in nonstoichiometric $YBa_2Cu_3O_{7-\delta}$ of different structural order

W. Bieger, G. Krabbes, P. Verges, M. Ritschel and J. Thomas

Institut für Festkörper- und Werkstofforschung Dresden e. V.
Helmholtzstr. 20, O-8027 Dresden, BR Deutschland

Abstract

Oxygen deficient $YBa_2Cu_3O_{7-\delta}$ powder samples with a well defined oxygen stoichiometry δ have been prepared at various temperatures and characterized by TEM, AC susceptibility and magnetization measurements. The interdependence between structural ordering and superconducting properties is discussed and a structural model based on a short-range ordering of oxygen in the Cu–O chains responsible for superconductivity is proposed.

1. Introduction

In order to further clarify the mechanism of superconductivity in cuprate based oxygen deficient perovskites the relationship between structure, defect ordering and superconducting properties remains important. Fuchs et al. [1] studied the dependence of T_c and H_{c2} on the oxygen deficiency δ in pure polycrystalline $YBa_2Cu_3O_{7-\delta}$ prepared by freezing of high temperature equilibrated samples (compare method (1) in section 2). However, it is recognized now that the only knowledge of the oxygen content is not sufficient to predict the electrical and magnetic properties of the material. These properties are significantly influenced by the preparation conditions especially the heat treatment (see e.g. [2]). The widely approved 60 K plateau of the $T_c(\delta)$ curves observed for samples prepared by the Zr gettering technique [3] was e.g. not closely confirmed when the samples were quenched from high temperatures in mercury [4]. The final properties depend on the oxygen defect ordering [5]. According to electronic structure calculations an ordered orthorhombic structure at least on a short length scale should be a necessary precondition for the superconductivity in such compounds [6]. Furthermore, various theoretical calculations using different models to describe the atomic interactions predict thermodynamically stable phases of oxygen deficient ordered structures (ortho II, ortho III) below 600 K (see e.g. [7]).

The present paper intends to be a contribution towards a further understanding of the experimental and structural parameters influencing the superconductivity in $YBa_2Cu_3O_{7-\delta}$. In addition to [1] its purpose is a proceeding clarification of the influence of annealing time and annealing temperature ("entropic" contribution [8]) on the oxygen atom ordering and on the superconducting properties of $YBa_2Cu_3O_{7-\delta}$ powder samples with fixed oxygen stoichiometry δ. The interdependence of atomic structure and superconductivity will be discussed.

Because the formation of ordered structures, which are studied by TEM, is preferentially observed at low temperature annealed samples the final heat treatment was usually carried out below 400°C. AC susceptibility as well as magnetization in dependence on temperature have been measured to characterize the superconducting properties.

2. Experiments

$YBa_2Cu_3O_{7-\delta}$ powder was synthesized starting from intimately mixed stoichiometric amounts of Y_2O_3 (Merck, p.a.), $BaCO_3$ (P.P.H. Gliwice / Poland, p.a.) and CuO (Ferak, p.a.) by multiple heat treatments at 900 to 920°C for 16 h in air and grounding, followed by a 24 h annealing at 930°C in oxygen.

In order to adjust a well defined final oxygen content the following methods have been developed and applied:

(1) Quenching method: Tablets of $YBa_2Cu_3O_{7-\delta}$ powder were equilibrated at high temperatures in flowing oxygen gas. The high temperature equilibrium was frozen in by quenching in liquid nitrogen. As shown in Figure 1 this method is an appropriate and reproducible tool to produce $YBa_2Cu_3O_{7-\delta}$ samples with a well defined mean stoichiometry.

(2) Homogenization method: $YBa_2Cu_3O_{7-\delta}$ samples the stoichiometry of which has been adjusted by

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method (1) were post-annealed for several days in closed silica ampoules at a certain temperature. In order to avoid changes of the oxygen content the free volume including pores was less than 0.1 cm^3/g.

(3) Isopiestic method: The oxygen content of the $YBa_2Cu_3O_{7-\delta}$ sample is adjusted in a two-zone equipment. The sample is held at the desired temperature T_1 (usually below 400°C) whereas the oxygen partial pressure $p(O_2)$ is controlled by a Cu_2O/CuO mixture as oxygen buffering system held at T_2. Hereby, $p(O_2)$ is chosen from the p–T–δ relationship for $YBa_2Cu_3O_{7-\delta}$ (see e.g. [9]) and T_2 for the buffer follows from the well known decomposition pressure for CuO.

(4) Controlled oxidation: Samples of $YBa_2Cu_3O_{7-\delta}$ with $\delta = 1.00 \pm 0.02$ were reproducibly synthesized by a 16 h annealing in flowing argon at 750°C. Such prepared tablets were put into a Bourdon manometer of known free volume together with the necessary amount of oxygen gas and sealed. Now, the oxygen absorption process of the sample at the desired temperature up to the formation of the final δ value can be determined by total pressure measurements.

The mean oxygen content of the resulting samples was controlled by iodometric titration. Bright field images and electron diffraction patterns characterizing the microstructure have been examined using a JEM-200 CX. The AC susceptibility dependence on temperature was determined in a susceptibility measurement equipment at magnetic fields of $1*10^{-5}$ T and $3*10^{-4}$ T and a frequency of 82 Hz. The magnetization $m(H)$ of the samples was measured with a vibration magnetometer VSM 3001 up to 8 T at several temperatures.

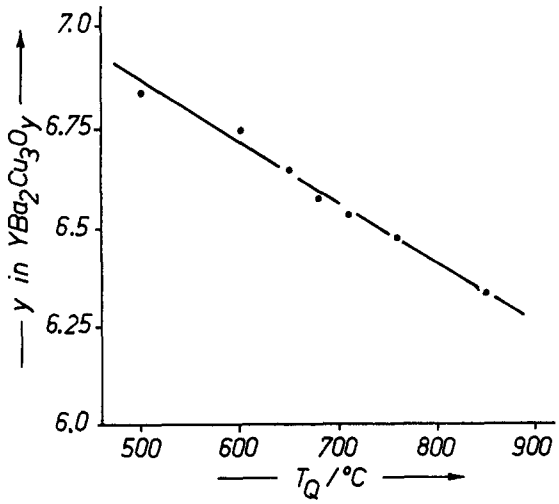

Figure 1. Quenching method. Dependence of oxygen stoichiometry (y= 7-δ) determined by iodometric titration on equilibration temperature T_Q at $p(O_2)= 1*10^5$ Pa

3. Results

3.1. TEM investigations

The structure of $YBa_2Cu_3O_{7-\delta}$ samples the oxygen stoichiometry δ of which had been adjusted by the different methods described in section 2 were studied. Independent of δ, particles prepared by the quenching method (1) did not show any superstructure signal. The oxygen mobility at the temperatures where the samples had been equilibrated was to high and, therefore, the range of possible partial ordering is smaller than the size region of electron scattering.

However, when the same samples with $\delta \approx 0.5$ were subsequently annealed at $T < 400$°C for 1 to 2 days according to method (2), streaks have been observed in the [001] patterns which indicate an at least partial 2 a ordering parallel to the a–b basal plane of the $YBa_2Cu_3O_{7-\delta}$ unit cell. When the temperature of the subsequent treatment is further decreased to 250°C the 2a signals become sharp spots thus indicating a well correlated ordering (Figure 2). Analogeous results have been obtained when the oxygen content was adjusted by methods (3) and (4).

Samples, the stoichiometry of which significantly differs from $\delta \approx 0.5$ did not show any superstructure signal. Twinning was usually observed independent of sample history and oxygen content. Therefore, the formation of long-range ordered superstructures is primarily dependent on temperature and oxygen stoichiometry.

3.2. Magnetic measurements

It was proved in [2] that the χ'(T) transition of $YBa_2Cu_3O_{7-\delta}$ can be split into an intragrain contribution which is not dependent on weak fields and a H-dependent intergrain one. Unexpectedly, it was observed that a sharp transition into the superconducting state is only typical for as quenched samples which had been equilibrated at $T \geq 400$°C.

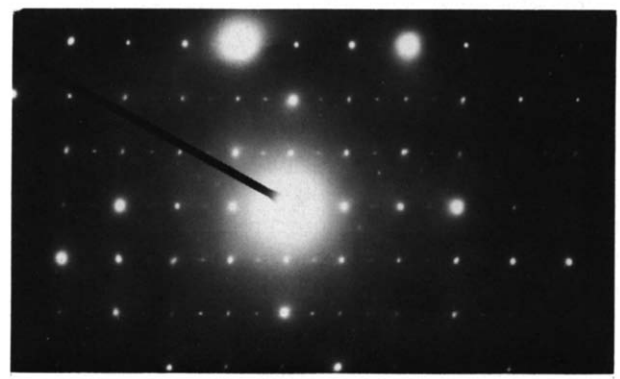

Figure 2. TEM [001] pattern of $YBa_2Cu_3O_{7-\delta}$ ($\delta \approx 0.5$) sample, prepared by controlled oxidation at 380°C, indicating 2a superstructure spots

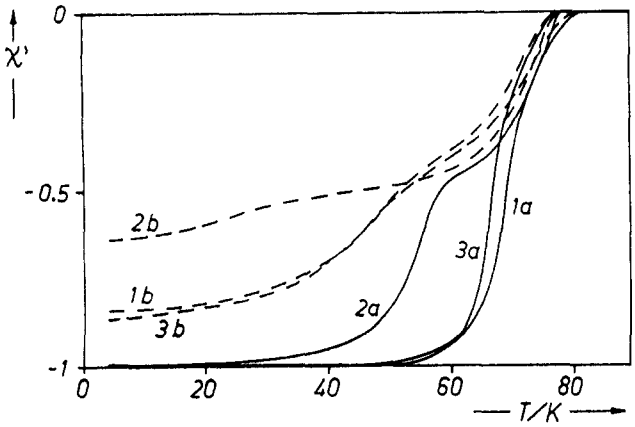

Figure 3. AC susceptibility vs. temperature plots of $YBa_2Cu_3O_{7-\delta}$ samples (δ= 0.27) at a field of (a) H = $1 * 10^{-5}$ T and (b) H = $3 * 10^{-4}$ T [(1): Quenched sample (Equilibration at 600°C); (2): Annealed sample (24 h at 380°C); (3): Annealed sample (24 h at 480°C)]

Polycrystalline samples of $YBa_2Cu_3O_{7-\delta}$ with δ = 0.27 (the oxygen content of which had been adjusted by a 16 h heat treatment at 600°C in O_2 and quenching according to Figure 1) were annealed for 24, 48, 92, 192 and 384 hours at different temperatures in closed ampoules (Homogenization method (2)). The χ'(T) curves of the quenched sample as well as the 24 h annealed samples at 380°C and 480°C are represented in Figure 3. The onset temperature as well as the first part of all transitions is nearly independent of sample history indicating the intragrain contribution to the superconductivity as discussed in [1]. The transitions of the quenched and the 480°C annealed samples are very similar and sharp at H= $1 * 10^{-5}$ T. An analogeous behaviour is found when the sample is annealed at T>480°C. The sample which had been annealed at 380°C (as well as all other samples treated at T<380°C) behaves quite different: Already at H= $1*10^{-5}$ T the two contributions of the transition can be clearly distinguished and the intergrain contribution completely vanishes at H= $3 * 10^{-4}$ T. A significant influence of the annealing time could not be reproducibly determined. Furthermore, samples the oxygen content of which had been adjusted by methods (3) and (4) behave similar to that of the homogenization technique (2).

In Figure 4, the current densities $j_{c,m}$ of differently post-annealed $YBa_2Cu_3O_{7-\delta}$ (δ= 0.27) samples derived from the magnetization curves $m(H)$ have been represented as functions of H and T. According to the Bean model, $j_{c,m}$ is approximately calculated via $j_{c,m} = 30 * \Delta m / V d_m$, where Δm is the difference between the two branches of the magnetization loop at

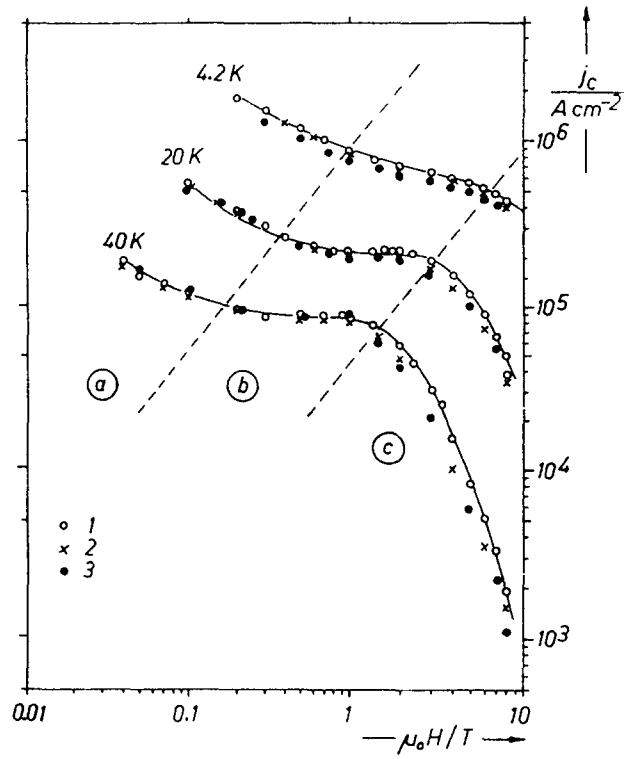

Figure 4. Magnetization current densities of differently prepared $YBa_2Cu_3O_{7-\delta}$ samples (δ=0.27) vs. magnetic field strength at various temperatures [(1): Quenched sample (Equilibration at 600°C); (2): Annealed sample (24 h at 380°C); (3): Annealed sample (24 h at 480°C)]

a given field H. V and d_m characterize the superconducting volume and the diameter of the current loops, respectively. In Figure 4, the real dimensions (mean diameter $\approx$ 20 μm) of the grains have been inserted into the above formula. At weak fields ($\mu_0 H$ < 1 T, part (a) in Figure 4) the intragrain j_c of all samples show a $H^{-\frac{1}{2}}$ dependence indicating an usual pinning mechanism. The plateau in the mean part of the curves (b) may be caused by small regions within the inhomogeneous grains which become non-superconducting and raising with increasing magnetic field. These domains may act as additional pinning centres. When H is further raised, a strong decrease of j_c is observed (part (c) in Figure 4). The reason of this behaviour becomes intelligible by considering the derivative dm/dH measured at the reversion point of the field which decreases with increasing temperature and magnetic field strength by nearly two orders of magnitude. Because the geometry function $G(d_m)$ in the formula $dm/dH = G(d_m) * V$ is limited by $1 < G(d_m) < 1.5$ in our experiments, the observed j_c decrease can be only explained by a reduction of the superconducting

volume. Consequently, it can be concluded that the critical field H_{c2} is already exceeded in many grains of the superconducting phase at the regarded high magnetic fields (H_{c2} of an as quenched sample was determined to be about 1.5 T at 40 K [1]). Therefore, part (c) in Figure 4 does not longer represent the intragrain j_c.

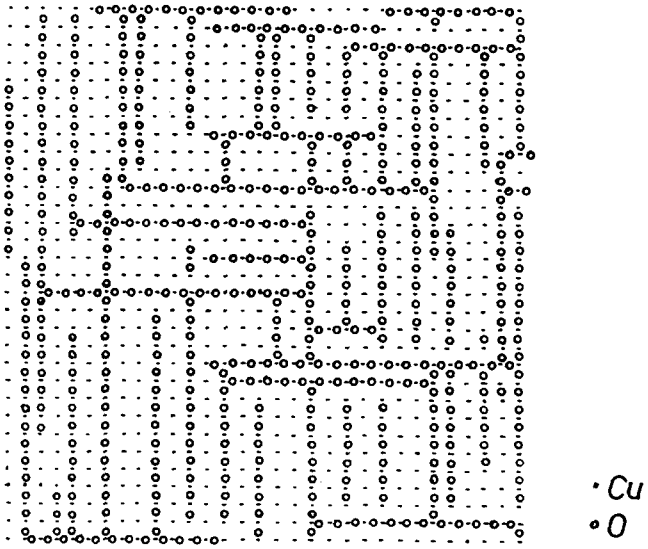

Figure 5. Proposed schema of Cu–O chains in short range ordered $YBa_2Cu_3O_{7-\delta}$ with $\delta = 0.5$

4. Discussion

A dominant influence of preparation conditions on structure and properties of differently post-annealed isostoichiometric $YBa_2Cu_3O_{7-\delta}$ samples is recognized by considering the $\chi'(T)$ transitions. The heat treatment especially affects the weak link behaviour. $YBa_2Cu_3O_{7-\delta}$ samples annealed at $T < 400°C$ usually possess regions with definitely ordered Cu–O chains but just the same samples do not show a sharp transition into the superconducting state. On the other hand, the transition widths of samples equilibrated at high temperatures are very small but no ordering of oxygen deficiencies can be observed although the mean oxygen deficiency is exactly the same as in the above mentioned case. Because at least partial ordering of oxygen vacancies is a necessary precondition for superconducting behaviour [6] the distribution of vacancies in high-temperature equilibrated samples is assumed to be ordered but only on a short length scale as it is schematically illustrated in Figure 5 for an assumed stoichiometry $\delta = 0.5$. Monte Carlo calculations also predict the occurrence of similar structures [10].

The distinct dependence of properties and structure on the preparation conditions seems to be caused by a propagating ordering process which proceeds at decreasing annealing temperatures where domains of increasing size with superconducting properties will be formed besides weakly superconducting domains which determine the intergrain behaviour.

Intragrain properties are expected to be influenced by structural ordering phenomena. From magnetometer measurements a slight influence (by a factor ≈ 2 at 40 K) of the degree of ordering is observed, but it becomes clear that the properties in higher fields are much more determined by the general inhomogeneities in the grains.

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References

1 G. Fuchs, A. Gladun, S.-L. Drechsler, R. Müller, M. Ritschel, G. Krabbes, N. Koppetzki and A. Gilewski, phys. stat. sol. (b) 159 (1990) 797
2 G. Krabbes, W. Bieger, J. Thomas, P. Verges and H. Lütgemeier, Physica C 190 (1991) 141
3 R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak and D. Werder, Phys. Rev. B 36 (1987) 5719
4 C. Namung, J. T. S. Irvine and A. R. West, Physica C 168 (1990) 346
5 J. D. Jorgensen, D. G. Hinks, P. G. Radaelli, Shiyon Pei, P. Lightfoot, B. Dabrowski, C. U. Segre and B. A. Hunter, Physica C 185–189 (1991) 184
6 M. Gupta and R. P. Gupta, Physica C 185–189 (1991) 851
7 L. T. Wille, A. Berera and D. de Fontain, Phys. Rev. Lett. 60 (1988) 1065; V. E. Zubkus, S. Lapinskas and E. E. Tornau, Physica C 166 (1990) 472; G. Ceder, M. Asta and D. de Fontain, Physica C 177 (1991) 106
8 R. J. Cava, A. W. Hewat, E. A. Hewat, B. Batlogg, M. Marezio, K. M. Rabe, J. J. Krajewski, W. F. Peck Jr. and L. W. Rupp Jr., Physica C 165 (1990) 419
9 G. Krabbes, G. Auerswald, A. Bartl, H. Eschrig, B. Lippold, M. Ritschel, H. Vinzelberg, E. Wolf and U. Wiesner, Cryst. Res. Technol. 23 (1989) 1161
10 M. Ohkubo and T. Hioki, Physica C 185–189 (1991) 921