Investigation of a Peaked Feature in the Magnetic Susceptibility of $YBa_2Cu_3O_{6.30}$ Samples

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Z. Naturforsch. **58a,** 546 – 550 (2003); received July 21, 2003

The static magnetic susceptibility of two different $YBa_2Cu_3O_{6.30}$ samples has been measured at different fields in the range 2 – 300 K, using a superconducting quantum interference device magnetometer; one sample has been prepared by oxygen intercalation, the other one by deintercalation. The susceptibility shows a peak near 45 K in both samples, which depends on the field and the magnetic history. The susceptibility of semiconducting and superconducting compounds, with an oxygen content $O_{6.20}$ and $O_{6.41}$, respectively, has also been investigated. The presence of the peak in the $YBa_2Cu_3O_{6.30}$ samples has been explained by the combined effect of regions with a Curie-like behaviour and superconducting regions. The origin of these regions is discussed.

Key words: High T_c Superconductors; Magnetic Susceptibility; Yttrium Barium Copper Oxides; SQUID Magnetometry.

1. Introduction

A characteristic feature of the cuprate high-T_c superconductors (HTSC) is the strong dependence of their magnetic and superconduction properties on the number of holes (h) in the $Cu(2)O_2$ planes [1 – 4]. The long-range antiferromagnetic order at low-doping ($h < 0.02$) and the superconduction at high doping ($h > 0.05$) are clearly observed for all HTSC's [1, 3]. The transient region ($0.02 < h < 0.05$), enclosing the vanishing of antiferromagnetism (AF) and the emergence of superconductivity (SC), still remains unclear. A coexistence of SC with a novel spin-glass phase has been experimentally evidenced by neutron scattering [5], DC magnetization [6], muon spin relaxation (μSR) [7 – 8] and nuclear quadrupole resonance [9] in the $La_{2-x}A_xCuO_4$ (A = Sr, Nd) system and by μSR [8] in the $Y_{1-x}Ca_xBa_2Cu_3O_{6.1}$ system. For the $YBa_2Cu_3O_{6+x}$ (YBCO) compounds this transient regime, corresponding to $0.2 < x < 0.4$, is not readily accessible since the hole transfer from the $Cu(1)O_x$ chains to the $Cu(2)O_2$ planes is rather complex and depends critically on the oxygen ordering and content [10]. This introduced an uncertainty in many earlier studies of the phase diagram of the YBCO system, due to the difficulty in preparing samples with low oxygen content and the reproducible oxygen order conditions in the mostly empty $Cu(1)O_x$ chains. We have developed a topotactic-like technique for processing oxygen equilibrated and ordered polycrystalline pairs of YBCO samples suitable for this purpose, *i.e.* of well defined oxygen order conditions [11].

The aim of this work is to investigate the DC magnetic susceptibility in the AF-SC transient region on polycrystalline YBCO samples. We investigated a pair of $YBa_2Cu_3O_{6+x}$ samples (x = 0.30) prepared with the topotactic-like technique by intercalation and disintercalation of the oxygen; two samples with a larger (x = 0.41) and smaller (x = 0.20) oxygen content were also studied. The measurements, performed with a superconducting quantum interference device (SQUID) magnetometer, reveal an irreversibility temperature identified by the splitting of the zero field cooling (ZFC) and field cooling (FC) DC magnetization curves. The observed behaviour is discussed.

2. Experimental Procedure

The $YBa_2Cu_3O_{6+x}$ samples under investigation (x = 0.20; 0.30 and 0.41) were prepared by an oxygen intercalation/deintercalation process in a topotactic-like way. In this technique the fully oxygenated and reduced ($x \sim 1$ and $x \sim 0$) end-terms, annealed into a sealed vessel in vacuum, act as oxygen donor and acceptor, respectively, in order to arrive at the final oxygen content (x) in both deintercalated ($[D]_x$) and intercalated ($[I]_x$) samples.

In details, the bulk polycrystalline $[D]_x$ and $[I]_x$ samples under investigation were prepared in a reproducible way, starting with fully oxygenated $x = 0.96$ bar-shaped samples of $3.0 \cdot 2.0 \cdot 14.0\ \text{mm}^3$ (weight about 0.5 g), prepared by a conventional solid-state reaction and sintering, and with fully reduced ($x = 0.07$) samples obtained from the former by dynamic vacuum annealing at 650 °C. The oxygen content in the samples was estimated with an accuracy of 0.02 oxygen atoms per formula unit, using iodometric and weight-loss analyses. A number of stoichiometric end-terms bars were equilibrated at a given temperature (T_e = 670 °C) for 1 day, slow by cooled at 0.2 °C/min to T_s = 75 °C, then order-stabilised at this temperature for 3 days and finally cooled (0.2 °C/min) to room temperature. The sample mass loss or gain is due solely to a change in oxygen content in the $Cu(1)O_x$ plane [12], and excellent agreement between the calculated and experimental oxygen content at equilibrium was systematically obtained. This topotactic-like procedure yields pairs of YBCO specimens under equilibrium conditions with equal oxygen content and thermal history. In this work we examined the $[I]_{0.30}$, $[D]_{0.30}$, $[I]_{0.20}$ and $[D]_{0.41}$ samples.

The X-ray diffraction patterns, collected using a θ-2θ conventional powder diffractometer (Siemens D501) with Cu-K_α radiation, did not show the presence of impurities of other phases in the samples investigated.

AC resistive measurements were carried out by the standard four-probe method at 33 Hz and current density of 0.01 A/cm^2. The pair samples with $x = 0.30$ show a semiconducting behaviour in the temperature range investigated (10 – 300 K). The same behaviour is evidenced by the $[I]_{0.20}$ sample. The $[D]_{0.41}$ sample is a superconductor with a resistive critical temperature of (43.4 ± 0.1) K, measured at zero resistivity.

The measurements of static magnetization have been performed with a SQUID magnetometer (Quantum Design MPMS5) equipped with a superconducting magnet generating fields up to 5 T. The measurements have been performed on a piece of sample with mass 5 – 80 mg at temperatures ranging from 2 K to 300 K, with different values of the magnetic field from 25 G to 2000 G. The zero field cooling and field cooling magnetizations have been measured during the warming run of the samples.

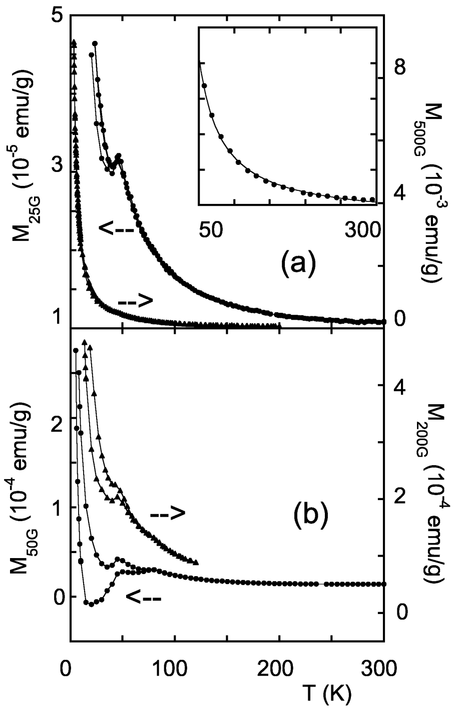

Fig. 1. (a): Magnetization M of the intercalated $[I]_{0.30}$ sample at 25 G (circles) on the left ordinate (M_{25G}) and at 500 G (triangles) on the right ordinate (M_{500G}) vs. temperature. (b): Magnetization of the $[D]_{0.30}$ sample at 50 G (circles) on the left ordinate (M_{50G}) and at 200 G (triangles) on the right ordinate (M_{200G}). The zero field cooling (ZFC) curves (lower curve after separation) and field cooling (FC) ones are shown. The inset of (a) shows the magnetization at 25 G in the region of the fit (50 – 300 K); the experimental data (circles) and the fit curve (solid line) are shown.

3. Results

Fig. 1a shows the static magnetization of the $[I]_{0.30}$ sample at two different fields; the ZFC and FC curves are plotted. The value of the susceptibility at room temperature (295 K) is $(4.31 \pm 0.05) \cdot 10^{-7}$ emu/g. The magnetization curves recorded at 25 G show a maximum near 45 K; this maximum is not present in the corresponding curves recorded under applied fields of 500 and 2000 G. Moreover, the ZFC and FC curves are separated below 45 K. Therefore the susceptibility depends on the field and on the magnetic history in the region of the peak and at lower temperatures.

Fig. 1b shows the magnetization of the $[D]_{0.30}$ sample with the ZFC and FC curves for two fields; the value of the susceptibility at 295 K is $(2.79 \pm 0.05) \cdot$

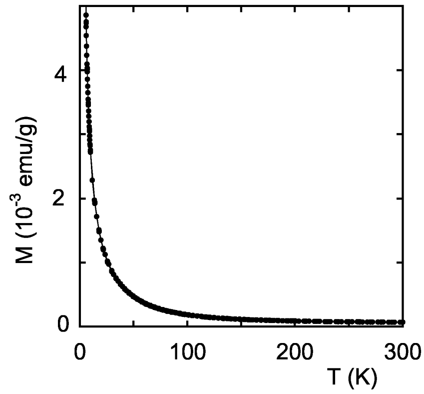

Fig. 2. Magnetization of the $[I]_{0.20}$ sample at 200 G vs. temperature. The ZFC and the FC curves overlapp.

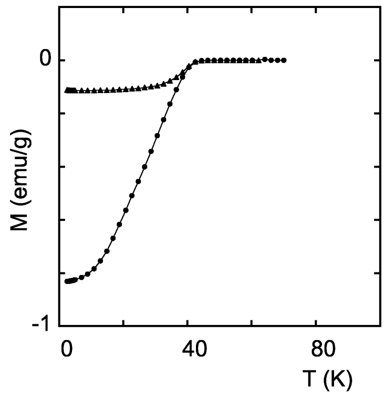

Fig. 3. Magnetization of the deintercalated $[D]_{0.41}$ sample at 100 G vs. temperature. The shielding curve (circles) and Meissner curve (triangles) are shown.

10^{-7} emu/g. The curves at 50 G show a peak at 45 K and a 2nd maximum at 80 K; these features are smoothed at 200 G, showing a dependence on the field. The separation of the ZFC and FC curves appears below 80 K in the magnetization with the lower field.

In Fig. 2 the magnetization of the semiconducting $[I]_{0.20}$ sample at 200 G is shown; the value of susceptibility at 295 K turns out to be $(3.49 \pm 0.05) \cdot 10^{-7}$ emu/g. The ZFC and FC curves coincide, and there is no dependence of the susceptibility on the field up to 20 K.

Fig. 3 plots the shielding and the Meissner magnetization of the superconducting $[D]_{0.41}$ sample at 100 G; the value of susceptibility at 70 K is $(9.48 \pm 0.05) \cdot 10^{-7}$ emu/g. The onset temperature of the superconductive transition, determined by the diamagnetic transition, is (53 ± 1) K, and the shielding susceptibility reaches a value of 4% of the susceptibility of the perfect diamagnet.

4. Discussion

The strong increase of the magnetization at low temperatures in the non-superconducting samples must be analyzed. As it concerns the $[I]_{0.30}$ sample, a Curie-like behaviour can be searched at temperatures higher than the peak; we made a fit of the data at different fields to the function

$$\chi = \chi_0 + C/(T - T_c) \tag{1}$$

for 50 K$< T <$ 300 K [9]. We found a Curie temperature (T_c) of (19 ± 1) K and a Curie constant (C) of $(3.0 \pm 0.1) \cdot 10^{-5}$ emu/g·K for the different fields. Moreover the susceptibility below 19 K, measured at 25, 50, 500, and 2000 G, is field dependent. The dependence on the field suggests that the behaviour at low temperature is dominated by the presence of ferromagnetic impurities which usually are formed in the preparation of ceramic YBCO systems; the value of T_c (19 K) permits to identify this impurity as the ferromagnetic $BaCuO_2$ compound [13], which has been observed as impurity in YBCO systems [13]. The amount of $BaCuO_2$ is about 1.7% of the mass, as deduced by the value of C [13]. The same procedure, applied to the $[D]_{0.30}$ sample, leads to a value of the $BaCuO_2$ content of about 1.6% of the mass. As it concerns the $[I]_{0.20}$ sample, by applying the same procedure we found a Curie temperature of (21±2) K, corresponding to the same kind of impurity within the experimental error; the amount is about 3.8% of the mass.

The hyperbolic contribution can be subtracted from the magnetization of the $[I]_{0.30}$ sample at 25 G and the $[D]_{0.30}$ sample at 50 G for temperatures up to the Curie temperature; the resulting data are shown in Fig. 4a and 4b, respectively. The value of the corrected susceptibility at 295 K is $3.3 \cdot 10^{-7}$ emu/g for the $[I]_{0.30}$ sample and $1.7 \cdot 10^{-7}$ emu/g for the $[D]_{0.30}$ sample. The behaviour at low temperature is dominated by a superconducting transition; a comparison with the susceptibility of the $[D]_{0.41}$ sample leads to an estimate of the volume of the superconducting region of about 0.3% and 0.5% in the $[I]_{0.30}$ and $[D]_{0.30}$ samples respectively. The superconducting component shows in the $[I]_{0.30}$ sample a transition onset temperature of (46 ± 1) K, and in the $[D]_{0.30}$ sample a transition onset temperature of (70 ± 1) K, followed by a sharp de-

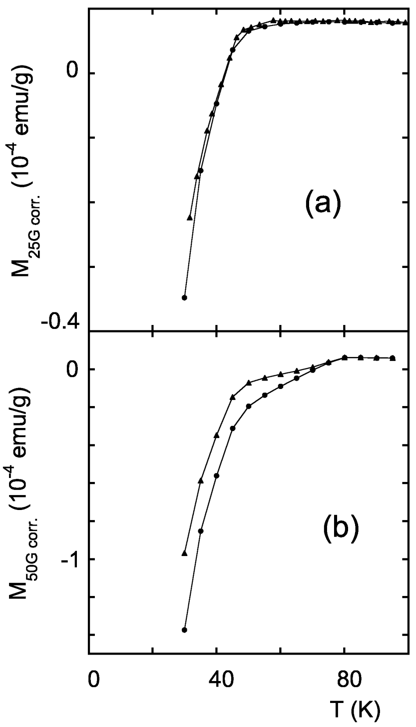

Fig. 4. (a): Magnetization of the $[I]_{0.30}$ sample at 25 G after subtraction of the Curie-like contribution up to 30 K ($M_{25G\ corr.}$) vs. temperature. (b): Magnetization of the $[D]_{0.30}$ sample at 50 G after subtraction of the Curie-like contribution ($M_{50G\ corr.}$). The ZFC curve (circles) and the FC curve (triangles) are shown.

crease of the susceptibility at (45 ± 1) K, due to superconducting regions with lower T_c. It is difficult to make statements about the origin of this superconducting region in the $YBCO_{6.30}$ samples; it is possible that this region is due to a slightly different $Cu(1)O_x$ chain ordering through the bulk [10].

The magnetization of the $YBCO_{6.30}$ samples is fully explained by the combined effect of ferromagnetic impurities and superconductiong regions; the peak at low fields is generated by the Curie-like behaviour combined with a superconducting transition; in the $[D]_{0.30}$ sample the appearance of two peaks depends on the two superconducting transition temperatures. At the maximum susceptibility, the ZFC and FC curves separate because the ZFC and FC susceptibilities describe the shielding and Meissner effect of the superconducting regions. The disappearance of the peaks at higher values of the field is due to the suppression of the superconductivity (at a given temperature) by the magnetic field.

Therefore in the $[I]_{0.30}$ and $[D]_{0.30}$ samples, no feature of the magnetization which can be ascribed to a spin-glass ordering have been observed according to recent μSR measurements [14], unlike the DC magnetization observed in $La_{1.96}Sr_{0.04}CuO_4$ [6]. The presence of a peak depending on the field and on the magnetic history has a different origin, as above described. However, we remark that possible spin-glass ordering below 45 K could be masked both by the small superconducting regions and by the ferromagnetic impurities observed.

5. Conclusions

The measurements performed with a SQUID magnetometer for two different $x = 0.30$ samples reveal a peak close to 45 K in the DC susceptibility curves. The observed behaviour is explained by the presence of superconducting regions, involving less than 1% of the mass of the samples. No spin-glass ordering has been observed. The presence of a peak, depending on the field and the magnetic history, has the different origin described above.

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