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Normal-state susceptibility versus oxygen content in the $YBa_2Cu_3O_x$ and $Y_2Ba_4Cu_7O_y$ superconducting phases.

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Abstract

Extensive measurements of the normal-state susceptibility have been performed on high quality $YBa_2Cu_3O_x$ (123) and $Y_2Ba_4Cu_7O_y$ (247) superconducting samples with various oxygen contents. The behaviour of $\chi_g(T)$ is similar to that of the other high-T_c oxides where the critical temperature can be varied like $La_{2-x}Sr_xCuO_{4-y}$ [1], $Bi_2Sr_2CaCu_2O_{8+\delta}$ [2], $Tl_2Ba_2Cu_1O_{6+\delta}$ [3], ... Near the optimum hole doping where T_c is maximum, the normal-state susceptibility becomes temperature independent. Below this optimum (with a lower oxidation), the slope $\partial\chi_g/\partial T$ is positive. This can be attributed to 2 dimensional, S=1/2 Heisenberg antiferromagnetic (AF) short-range order. If the oxidation decreases, 6.4<x<6.6 in the $YBa_2Cu_3O_x$ and y<14.5 in the $Y_2Ba_4Cu_7O_y$ phase, a low-T upturn appears which suggests incipient 3 dimensional order. In contrast to the 247 system where all samples are superconducting, the 123 ceramics with about x<6.4 are insulating. No break in $\chi_g(T)$ was detected at the Néel temperature T_N (3D long range AF order) in these samples. Above the optimum doping (with a larger oxidation), the slope is negative. It seems that only in the 123 system can the overdoped superconducting state be obtained (x>6.96). A sample with x=6.98 presents a negative slope of $\chi_g(T)$. However, already 0.1% by volume of the potential impurity $BaCuO_2$ could change the sign of the slope.

1. Introduction

The normal-state susceptibility is an important tool to investigate the magnetic and electronic properties of metallic phases. Unfortunately, $\chi_g(T)$ critically depends on the purity of the samples. For example, a very small content of $BaCuO_2$ in a $YBa_2Cu_3O_x$ sample can mask the intrinsic properties. In the present work, we show extensive measurements without any corrections for Curie moments or potential second phases of high purity and homogeneous $YBa_2Cu_3O_x$ (123) and $Y_2Ba_4Cu_7O_y$ (247) samples with different oxygen contents. The critical temperature ranges from 0 to 92 K and 30 to 95 K in the 123 and 247 phases, respectively.

2. Sample preparation

High quality $YBa_2Cu_3O_x$ and $Y_2Ba_4Cu_7O_y$ batches were prepared at high temperature, 980-990 °C and 1010-1020 °C, under 1 bar and 20 bar oxygen pressure, respectively. The samples contain grains larger than typically 20 μm. A very small amount of CuO and $BaCuO_2$ (123 samples) or $Ba_2Cu_3O_x$ (247 samples) was detected in optical and SEM investigations (< 0.5% by volume). Samples prepared in the same batch contain the same amount of impurity phases. To change and homogenize the oxygen concentration, each sample was annealed at a different temperature and oxygen pressure (10^{-6}-100 bar). These long final treatments were followed by quenching into liquid gallium. The oxygen concentration was determined by recording the mass change during the reduction of the samples in pure hydrogen flow at 900 °C. The lattice parameters of the samples are indicated in tables I & II. A more detailed description is given elsewhere [4, 5].

3. Experimental details

In all magnetic measurements we use the c.g.s. system where $B=H+4\pi M$ and $\chi_v=M/H=\rho\chi_g$. The a.c. susceptibility was measured in a magnetic field of 0.1 Oe rms at a frequency of 73 Hz. The Meissner flux expulsion $f=-4\pi\chi_v$ (field cooling) was measured using a r.f. SQUID magnetometer. The field of about 20 Oe was calibrated by means of a high purity Pb sphere in the Meissner state. A geometric demagnetisation factor D, depending on the sample shape, was systematically taken into account. The true susceptibility reads $\chi_g=\chi_g^m/(1-4\pi D\rho\chi_g^m)$, where χ_g^m is the measured susceptibility and ρ the X-ray density. The normal state susceptibility was measured with the same SQUID magnetometer in an external magnetic field of 20 kOe. No significant amount of ferromagnetic impurities was

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detected by means of Honda's method [6]. The result of $\chi_g(T)$ is given *without any correction*.

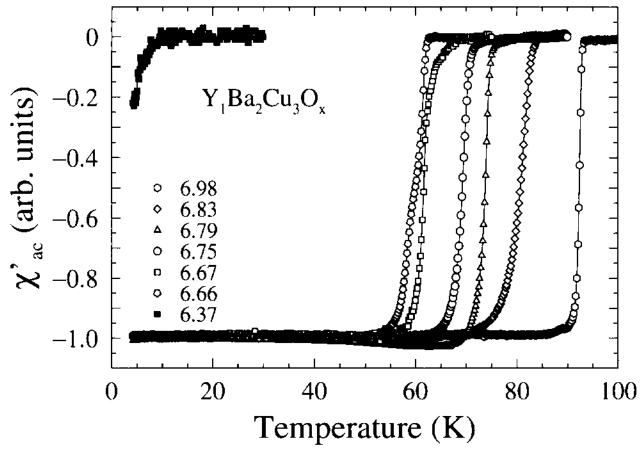

Figure 1: Superconducting transitions measured by a.c. susceptibility for the $YBa_2Cu_3O_x$ samples ($H=0.1$ Oe_{rms}). The legend gives the oxygen concentration x.

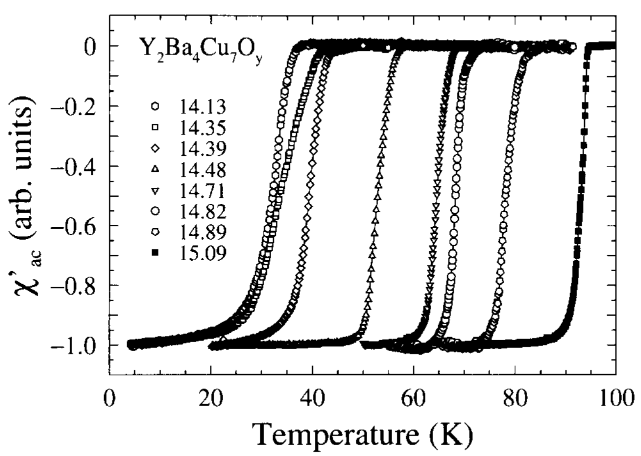

Figure 2: Superconducting transitions measured by a.c. susceptibility for the $Y_2Ba_4Cu_7O_y$ samples ($H=0.1$ Oe_{rms}). The legend gives the oxygen concentration y.

4. Determination of T_c

Figs. 1 and 2 show the superconducting transitions determined using the a.c. susceptibility experiment for our 123 and 247 samples. The sharpness of the transitions at any T_c is a consequence of the long annealing treatment and the final quench of the samples. Fig. 3 shows the critical temperature T_c versus the formal hole doping p (Cu^{2+p}) for both systems. The critical temperatures T_c and the percentage of Meissner flux expulsion f at low temperature of the samples used to measure $\chi_g(T)$ are listed in table I & II. The optimum of T_c is at x=6.96 in the 123 phase and does not seem to be attained in the 247 phase, considering that, in contrast to the other high-T_c systems, the slope $\partial\chi_g/\partial T$ of the normal-state susceptibility does not vanish even for y=15.09.

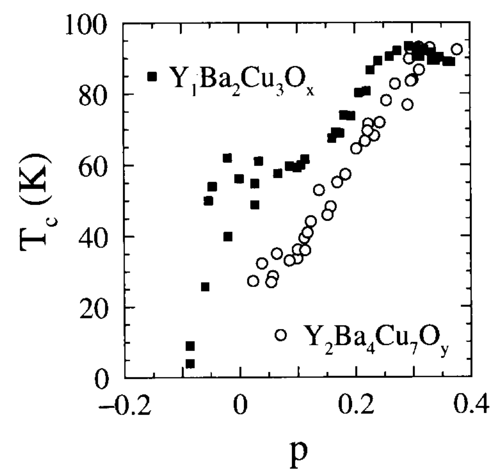

Figure 3: T_c (midpoint) vs. formal hole density p (per copper atom.).

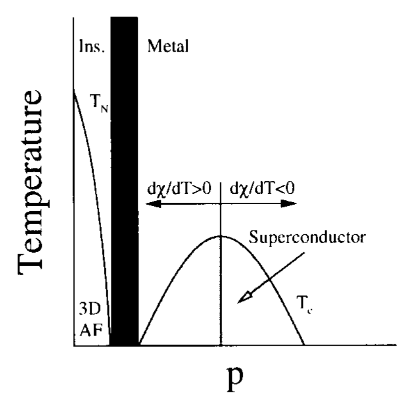

Figure 4: Schematic representation of the dependence of T_c and T_N vs. formal hole density p.

5. Normal-state susceptibility

In the $La_{2-x}Sr_xCuO_{4-y}$ system, neutron diffraction studies show 3D long range antiferromagnetic order (AF) in the non-superconducting region (p=x-2y<0.05). Above the Néel temperature T_N, the large intraplanar exchange coupling between copper moments in the CuO_2 planes ($J/k_B \approx 1000K$) only leads to 2D, S=1/2 Heisenberg AF short-range order. The magnetic susceptibility shows a peak at the 3D transition and a positive slope sufficiently above T_N. When the hole doping p increases, the system becomes metallic and superconductivity appears, the long range order is suppressed and only short range 2D interactions survive. At the approach of the optimum hole doping where T_c is maximum, the system changes over to a Pauli-like behaviour [7] and the slope of $\chi_g(T)$ vanishes. Fig. 4 summarizes the physical properties versus the hole doping p (Cu^{2+p}).

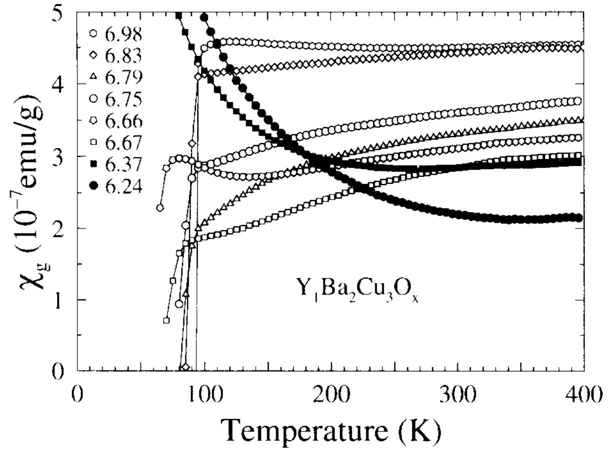

Figure 5: Susceptibility above T_c vs. temperature for different degrees x of oxidation in the $YBa_2Cu_3O_x$ phase.

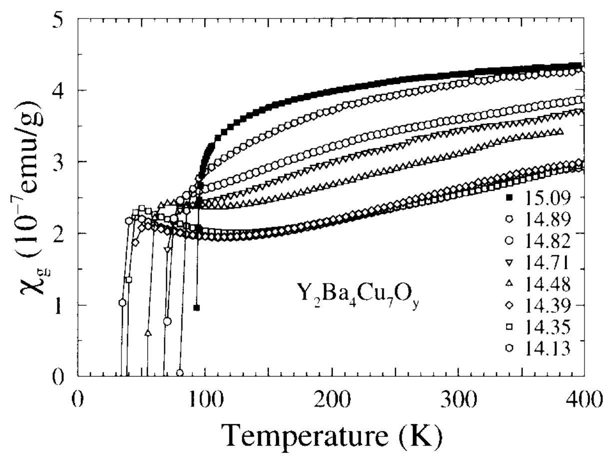

Figure 6: Susceptibility above T_c vs. temperature for different degrees y of oxidation in the $Y_2Ba_4Cu_7O_y$ phase.

Figs. 5 and 6 show the measurements of $\chi_g(T)$ for our 123 and 247 samples. Both systems seem to follow the same behaviour in their magnetic properties as the $La_{2-x}Sr_xCuO_{4-y}$ system. At the optimum hole doping and above the region where superconducting fluctuation contribute, the normal-state susceptibility becomes temperature independent. For lower oxidation, T_c decreases and $\chi_g(T)$ presents a positive slope. By analogy with the $La_{2-x}Sr_xCuO_{4-y}$ phase, we suggest that 2D short range AF order dominates the temperature dependence of χ_g in this region of oxygen content. If we continue to decrease the oxygen content, a low temperature upturn appears in both systems. This Curie-Weiss like contribution could be due to 3D AF correlations or localised magnetic moments. We cannot attribute this behaviour to the presence of impurities, because all samples originate from the same initial batch. In the $YBa_2Cu_3O_x$ phase, the samples become semiconducting or insulating when x drops below 6.4. Neutron investigations indicate 3D AF order in this region [8]. In contrast to investigations in grain aligned powders (H//c) [9], no break was seen at the Néel temperature. Attempts to obtain non-metallic 247 samples were not successful even for y as low as 14.13. All 247 samples are superconductors. The optimum T_c in the 123 phase occurs for x≈6.96 oxygen per formula unit (see ref [4]). Our $YBa_2Cu_3O_{6.98}$ sample should therefore be slightly overdoped and consequently, the slope of $\chi_g(T)$ should be negative. This is indeed observed in fig. 5. Note however that a hypothetical correction of $\chi_g(T)$ for only 0.1% by volume of $BaCuO_2$ in the sample would change the sign of the slope. The inversion of the curves for x=6.79 and x=6.75 in the sequence of the $\chi_g(T)$ curves for 123 may be explained by preferential orientation effects. Nakazawa and Ishikawa have found similar result in the 123 system [10].

Table I ($YBa_2Cu_3O_x$):

x	T_c (χ^{AC}, midpoint) (K)	f at 5 K (%)	χ_g(300 K) (x10^{-7} emu/g)	a (Å)	b (Å)	c (Å)
6.24	0	0	2.19	3.8586	3.8586	11.842
6.37	7 (onset)	-	2.84	3.8447	3.8693	11.763
6.66	60.0	42	3.11	3.8299	3.8790	11.734
6.67	61.6	34	2.84	3.8315	3.8778	11.738
6.75	69.2	30	3.60	3.8238	3.8826	11.719
6.79	73.7	33	3.31	3.8232	3.8860	11.713
6.83	80.7	25	4.51	3.8255	3.8824	11.719
6.98	92.4	43	4.50	3.8175	3.8896	11.682

Table II ($Y_2Ba_4Cu_7O_y$):

y	T_c (χ^{AC}, midpoint) (K)	f at 5 K (%)	χ_g(300 K) (x10^{-7} emu/g)	a (Å)	b (Å)	c (Å)
14.13	32.3	23	2.55	3.8467	3.8662	50.851
14.35	33.7	38	2.54	3.8468	3.8678	50.808
14.39	39.5	40	2.63	3.8450	3.8694	50.785
14.48	52.9	38	3.11	3.8425	3.8719	50.709
14.71	64.6	44	3.45	3.8379	3.8762	50.674
14.82	68.2	44	3.59	3.8366	3.8758	50.631
14.89	78.1	47	4.09	3.8339	3.8767	50.611
15.09	93.1	56	4.22	3.8302	3.8753	50.584

Tables I & II indicate the value of χ_g at 300 K for all samples studied in this work. If we assume that the van Vleck paramagnetic contribution is not significantly affected by the oxygen content in these two systems, the increase of χ_g(300 K) with oxygen concentration can be attributed to an increase of the Pauli paramagnetism which is proportional to the density of states at the Fermi level. Calorimetric measurements in the $YBa_2Cu_3O_x$ phase show that the maximum of the specific heat jump is at x=7.0 (rather than at the highest T_c, x=6.96) [11]. This fact also suggests an increase of the EDOS with hole doping.

The analysis of the superconducting fluctuation contribution to χ_g(T) for sample $Y_2Ba_4Cu_7O_{15.09}$ was presented elsewhere [12].

6. Conclusion

The normal-state susceptibility χ_g(T) versus hole doping in the $YBa_2Cu_3O_x$ and $Y_2Ba_4Cu_7O_y$ systems follows the same behaviour as in the other high-T_c superconductors where T_c can be varied like $La_{2-x}Sr_xCuO_{4-y}$, $Bi_2Sr_2CaCu_2O_{8+\delta}$ or $Tl_2Ba_2Cu_1O_{6+\delta}$. The optimum T_c is correlated with a vanishing $\partial\chi_g/\partial T$. Above or below, the slopes have opposite signs. The EDOS at the Fermi level increases with the oxygen concentration.

7. Acknowledgements

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References

1 D.C. Johnston, Phys. Rev. Lett. **62** (1989) 957
2 G. Triscone et al., Physica C **176** (1991) 247
3 C. Allgeier and J.S. Schilling, Physica C **168** (1990) 499
4 T. Graf et al., J. Less-Common Met., **159** (1990) 349
5 J.-Y. Genoud et al., Physica C **192** (1992) 137
6 K. Honda, Ann. Physik **32** (1910) 1027
7 D.C. Johnston, J. Mag. and Mag. Mat. **100** (1991) 218
8 J.M. Tranquada, A.H. Moudden, A.I. Goldman, P. Zolliker, D.E. Cox, G. Shirane, S.K. Sinha, D. Vaknin, D.C. Johnston, M.S. Alvarez, A.J. Jacobson, J.T. Lewandowski and J.M. Newsam, Phys. Rev. B **38** (1998) 2477
9 Y. Yamaguchi, M. Tokumoto, S. Waki, Y. Nakagawa and Y. Kimura, J. Phys. Soc. Japan **58** (1989) 2256
10 Y. Nakazawa and M. Ishikawa, Physica C **158** (1989) 381
11 J.W. Loram, J.R. Cooper and K.A. Mirza, Supercond. Sci. Technol. **4** (1991) S391
12 G. Triscone et al., Physica C **201** (1992) 1