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Magnetic properties of the $Tl_2Ba_2Cu_1O_{6+\delta}$ 90K superconductor

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Abstract

We have measured magnetic properties of high quality $Tl_2Ba_2Cu_1O_{6+\delta}$ 90 K tetragonal superconducting and orthorhombic metallic non-superconducting ceramics. The AC susceptibility shows distinct intra- and intergrain transitions down to H=0.004 Oe rms. The field cooling measurement at 20 Oe shows a sharp transition at 90 K and 50% of full flux exclusion at 5 K. At T>150 K, i.e. above the region where superconducting fluctuations contribute, the normal-state susceptibility is temperature independent and diamagnetic with a value of -5×10^{-8} emu/g. The intergrain critical current densities determined at B=1 T, using Bean's critical state model, are very low, 6×10^3 A/cm^2 at 5 K and below 1 A/cm^2 at 40 K.

1. Introduction

In many high-T_c superconductors where the critical temperature can be varied with hole doping like $YBa_2Cu_3O_{7-\delta}$ [1] or $Bi_2Sr_2CaCu_2O_{8+\delta}$ [2], the behaviour of the normal-state susceptibility vs. temperature follows an interesting empirical rule. At the optimum hole doping where T_c is maximum, $\chi_g(T)$ becomes temperature independent. Above or below, $\partial\chi_g/\partial T$ is negative or positive, respectively. The presently favoured picture to describe the temperature variation of the susceptibility of oxide superconductors takes into account intraplanar exchange coupling between copper moments, especially at low doping levels, and a gradual change over to Pauli-like behaviour. In this paper, we report on the magnetic properties of $Tl_2Ba_2Cu_1O_{6+\delta}$ (Tl-2201), both in the superconducting and normal states. In spite of the many structural contradictions, it seems that only the tetragonal phase of Tl-2201 can become superconducting [3]. The structure changes to orthorhombic symmetry in the oxidised state. The samples are metallic. No superconductivity in the latter state was observed down to 6 K.

2. Sample preparation

The samples were prepared using the high temperature, high pressure route (850-930 °C and 100 bar Ar, He or O_2). The complete description is given in an another contribution in this conference [3]. Some physical parameters are listed in table I.

3. Experimental details

The superconducting transitions were detected by means of a mutual inductance bridge working at a frequency of 80 Hz. The AC field amplitude was set at either 0.1, 0.01 or 0.004 Oe_{rms}. The Meissner effect (field cooling) was measured using a r.f. SQUID magnetometer with an external magnetic field of 20 Oe. The Meissner flux expulsion ratio $f=-4\pi\chi_v$ ($B=H+4\pi M$, $\chi_v=M/H=\rho\chi_g$) was evaluated using an effective sample volume given by m/ρ, where m is the sample mass and ρ the X-ray density (≈8.0 g/cm^3). A geometric demagnetization factor D (0.16 for the TK2-R sample), depending on the sample shape, was taken into account. With the same magnetometer, we have measured the magnetic hysteresis at 5, 10, 20, 30, 40 and 77 K. These measurements of M(H) were taken after zero field cooling from above T_c to the desired temperature. The normal-state susceptibility was measured with an external magnetic field of 20 kOe. No significant amount of ferromagnetic impurities was detected by means of Honda's method [4].

4. A.C. susceptibility and Meissner flux expulsion

Fig. 1 shows the result of the A.C. susceptibility at two fields (0.1 and 0.01 Oe) and the Meissner field cooling (FC) measurements of the TK2-R sample. The samples present a double transition. No significant difference between H=0.01 and 0.004 Oe was observed. The upper transition at 90 K does not give rise to any appreciable dissipation and its shape does not depend on the strength or the frequency of the AC field. The second

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Table I:

sample	T_c^{onset} (K)	$f=-4\pi\chi_v(5K)$ %	D	a (Å)	b (Å)	c (Å)
TM-850	91.1	43.9	0.12	a=b=3.8717		23.225
TK2-R	90.5	53.1	0.16	a=b=3.8686		23.223
TKO-930	-	-	-	5.4467	5.4911	23.144

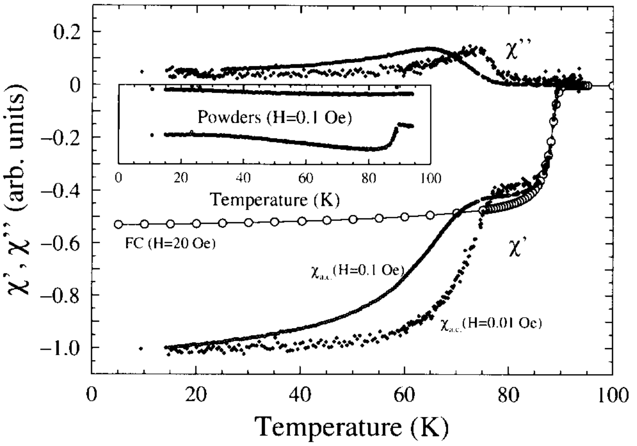

Figure 1: AC susceptibility (arbitrary units) of sample TK2-R at two levels of excitation: 0.1 Oe (squares) and 0.01 Oe (diamonds). Upper curves: imaginary part χ ''; lower curves: real part χ '. Open circle: field cooling (FC) susceptibility (Meissner effect) at H=20 Oe for the same sample TK2-R. The diamagnetism at 5 K corresponds to $-4\pi\chi_v$=53.1%. Inset: $\chi_{a.c.}$ measurement of the powdered sample versus temperature.

step between 60 and 80 K is accompanied by a broad dissipation peak. Its shape and position depend strongly on the amplitude of the AC field. This behaviour is characteristic for a granular superconductor with very weak intergranular coupling [5]. The $\chi_{a.c.}$ measurement at 0.1 Oe of the powders is also presented in the inset of fig. 1. A similar behaviour was observed in the related family of $Bi_2Sr_2CaCu_2O_{8+\delta}$ ceramics [2]. The upper step close to 90 K gives the intragrain transition temperature. Between this temperature and approximately 80 K, the sample effectively behaves as a superconducting powder. The magnetic field penetrates the sample because the surface cannot sustain the current required to completely screen the field. The lower transition is due to the weak inter-granular coupling (weak-link structure) and occurs when the critical current of the junctions between the superconducting grains exceeds the order of magnitude H/R, where R is the radius of the sample. The latter ratio amounts to only 0.1 A/cm^2, i.e. orders of magnitude below values typical for $YBa_2Cu_3O_7$ close to T_c. As expected, this step does not occur for powders (see inset of fig. 1). Although the microstructural origin of the weak-link behaviour of the bulk specimen is not clear, it could be attributed to the $Tl_2Ba_2O_5$ impurity phase which is occasionally detected at the surface of the superconducting grains, producing Josephson junctions. The low-temperature tail of the FC measurement follows the behaviour predicted for a granular sample with $r/\lambda(0)\approx30$, where r is the radius of the superconducting grains and $\lambda(0)$ is the penetration depth at T=0 [6]. Using the average grain size (5 µm) determined by optical micrographs, we obtain a rough estimate $\lambda(0)\approx1700$ Å, consistent with the values usually found in high temperature superconductors. An analysis of $\chi_{a.c.}$, FC and zero-field-cooling DC magnetization experiments, presented in another contribution [3], indicates that only half of the volume of the 2201 grains is actually superconducting.

5. Hysteresis measurements and critical currents

Fig. 2 shows the results M(H) for the TK2-R sample at T=5, 10, 20, 30 K. The 40 and 77 K loops do not present any significant hysteresis above 5 KOe. This complete reversibility almost 15 K below T_c is unusual. In terms of the "irreversibility line" concept, $Tl_2Ba_2CuO_6$ is more closely related to $Bi_2Sr_2CaCu_2O_8$ than to $YBa_2Cu_3O_7$.

The critical current is evaluated on the basis of Bean's critical model [7, 8]: $j_c\approx-3\ \{M_+(H)-M_-(H)\}/\varnothing$ where j_c is the critical current, $M_+(H)$ and $M_-(H)$ are the magnetizations measured with increasing and decreasing magnetic field, respectively, and $\varnothing$ is the diameter of the cylinder (in usual units, [A/cm^2], [emu/cm^3], and [cm]: $j_c\approx-30\ \{M_+(H)-M_-(H)\}/\varnothing$). Using the sample diameter $\varnothing$=0.2 cm, we obtain a macroscopic critical current density of about 6x10^3 A/cm^2 at 1 T and 5 K. By using the typical grain size of 5 µm, consistent with optical micrographs, we obtain $j_c=2.4\times10^6$ A/cm^2, a value that is more characteristic of intragranular critical current densities. Fig. 3 presents the calculated critical current j_c for different temperatures using nevertheless the macroscopic sample dimensions in Bean's formula. This result gives a strong lower limit for j_c. The approximate linearity of log(j_c) vs. H is characteristic of granular samples.

6. Normal-state susceptibility

Fig. 4 shows the normal-state susceptibility of a tetragonal sample (TM-850). Metallographic investigations show the 2201 phase and some traces of $Tl_2Ba_2O_5$ impurity phase. An evaluation of the percentage by volume (about 5%) is based on micrographs [3]. This is below the sensitivity threshold of X-ray diffraction patterns, which show only the 2201

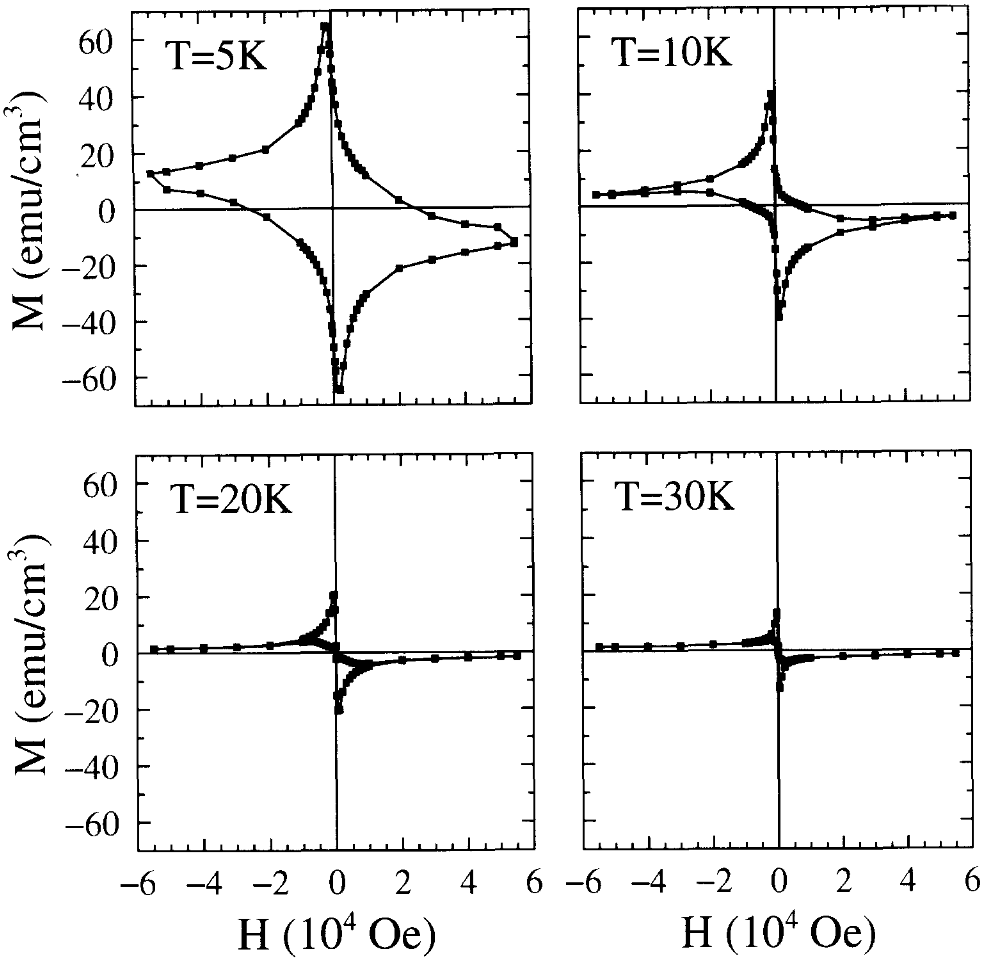

Figure 2: Magnetization cycles at 5, 10, 20 and 30 K for sample TK2-R.

main phase. Some CuO precipitates are sometimes seen at the grain boundaries. The susceptibility of the impurity $Tl_2Ba_2O_5$ phase is also presented in Fig. 4. It remains diamagnetic and almost constant from 100 to 400 K. The presence of this impurity results in a small downward shift of the total susceptibility with respect to the intrinsic contribution of the 2201 phase. The resulting intrinsic susceptibility of $Tl_2Ba_2CuO_6$ is shown as a full line in Fig. 4. It is small, diamagnetic, and essentially constant above 150 K. By analogy with the other high-T_c systems where the critical temperature can be varied appreciably with hole doping like $Bi_2Sr_2CaCu_2O_{8+\delta}$ [2], this temperature independence suggests that hole doping is optimal.

The total susceptibility $\chi_o(T=0)$ extrapolated from above 150 K is $-5x10^{-8}$ emu/g, or $-4x10^{-5}$ emu/mole-Cu. These values include a correction of $1x10^{-8}$ emu/g or $1x10^{-5}$ emu/mole-Cu for the $Tl_2Ba_2O_5$ impurity. Allgeier and Schilling previously found a similar value of about $-3x10^{-8}$ emu/g in a $Tl_2Ba_2Cu_1O_{6.10}$ (T_c=92 K) sample [9]. The diamagnetic core susceptibility of $Tl_2Ba_2CuO_6$ is $-2.29x10^{-7}$ emu/g if we assume that the oxidation states of the elements are $Tl^{+3}Ba^{+2}Cu^{+2}O^{-2}$ [10]. Owing to the Tl contribution, the core diamagnetism expressed per g-atom is somewhat larger than that of the YBaCuO family [11]. Moreover, the 2201 phase of the TlBaCaCuO system has a smaller fraction of copper atoms expected to be responsible for the paramagnetism. This fact probably explains why the total magnetic susceptibility is negative. The sum of the Pauli and van Vleck contributions amounts to $1.54x10^{-4}$ emu/mole-Cu, to be compared with $1.6x10^{-4}$ emu/mole-Cu for $YBa_2Cu_3O_7$ [11].

The rounding of $\chi_g(T)$ just above T_c is attributed to superconducting fluctuations. Based on Ginzburg-Landau theory, the expected behaviour of the fluctuation susceptibility can be written as $\chi_g(T)=-A\,|1-T/T_c|^{\alpha}$ where $\alpha=-0.5$ or -1 if the nature of the fluctuations is 3 dimensional or 2 dimensional. A fit rather suggests a value of $\alpha=-2$. The meaning of this observation is unclear. An analysis of the magnetic behaviour near T_c is given in another contribution at this conference [12].

The inset of fig. 4 shows the normal-state susceptibility of the 2201 orthorhombic phase, which is metallic but non-superconducting. The Curie-like behaviour corresponds to an equivalent 6% of Cu^{2+}

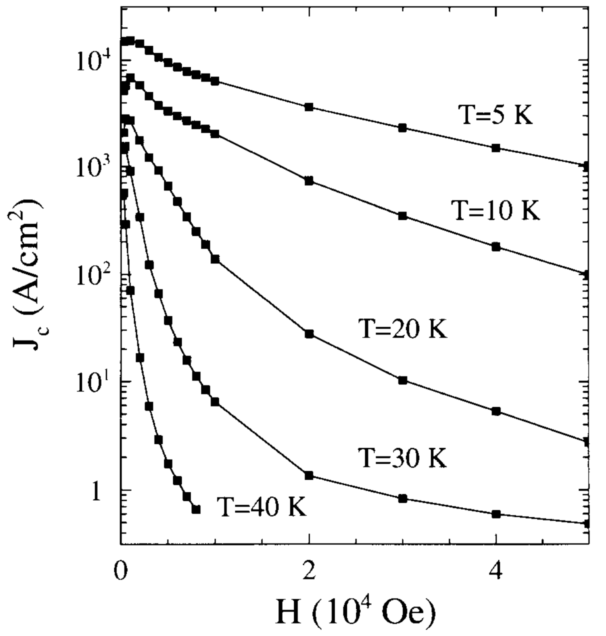

Figure 3: Macroscopic critical currents density vs. magnetic field at 5, 10, 20, 30 and 40 K determined with Bean's critical model.

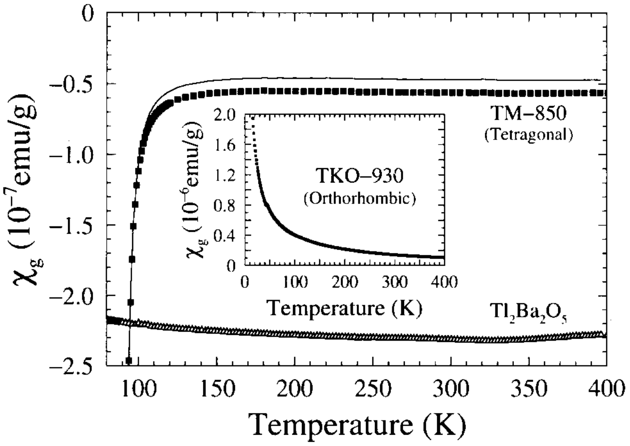

Figure 4: Normal-state susceptibility vs. temperature at H=20 kOe for sample TM-850. The lowest curve shows the susceptibility of the impurity phase $Tl_2Ba_2O_5$. The line indicates the intrinsic susceptibility of the 2201 (T_c=90K) phase. Inset: Magnetic susceptibility of the 2201 orthorhombic non-superconducting phase (sample TKO-930).

localized moments and appears as extrinsic. The break of χ_g at about 43.5 K is due to the β-γ transition of oxygen contained in the pores of the sample as observed in the cases of magnetic measurements in oxygen absorbed in graphite samples by Gregory [13]. The pores are sealed at high temperature during the heat treatment in oxygen at 100 bar. This anomaly due to the oxygen is also observed in orthorhombic and tetragonal samples elaborated at atmospheric pressure [14].

7. Conclusions

The normal-state susceptibility of the 90 K $Tl_2Ba_2Cu_1O_{6+\delta}$ superconductor is temperature independent above 150 K. By analogy with the other high-T_c systems [15, 16, 2, 1], this behaviour in the normal-state suggests that tetragonal $Tl_2Ba_2Cu_1O_{6+\delta}$ with T_c near 90 K is very close to the optimum hole doping. Due to a particular microstucture in the present ceramic samples, the intergrain critical current density is very low, even at liquid helium temperature. The quasi exponential decrease of j_c with magnetic field is characteristic of granular superconductors.

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