Thermodynamic signature of a phase transition in the pseudogap phase of YBa$_2$Cu$_3$O$_x$ high-$T_C$ superconductor

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received 6 March 2009; accepted in final form 24 June 2009
published online 24 July 2009

PACS 74.25.Dw – Superconductivity phase diagrams
PACS 74.72.Bk – Y-based cuprates
PACS 74.25.Ha – Magnetic properties

Abstract – We present here high-precision magnetisation measurements in polycrystalline YBa$_2$Cu$_3$O$_x$ samples, with oxygen content ranging from $x=6.19$ to $x=7.00$. By analysing the temperature derivative of the susceptibility, we found in the underdoped superconducting samples a singular point at a temperature corresponding to $T_{mag}$, the temperature below which polarised neutrons experiments have evidenced a symmetry breaking. We believe that this is a thermodynamic indication for the existence of a phase transition in the pseudogap state of underdoped YBa$_2$Cu$_3$O$_x$.

Introduction. – Understanding the theory of high-temperature superconductors remains one of the outstanding challenges in condensed-matter physics. One of the fascinating questions to address is the nature of the normal state in the underdoped part of the phase diagram, and in particular of the pseudogap which develops at the Fermi energy below a temperature $T^*$ well above the critical temperature $T_C$. Among the various theoretical proposals, an hypothesis is to consider the pseudogap as a precursor of the superconducting gap [1]. In this case pairing with short-range phase coherence occurs already at $T^*$ which is therefore more a crossover regime, while other models predict a genuine phase transition at this temperature, associated with some order parameter as for example proposed by Varma et al. [2–4]. The latter has recently received support from polarised neutron scattering experiments in underdoped YBa$_2$Cu$_3$O$_{7–\delta}$ (YBCO) [5,6] and in HgBa$_2$CuO$_{4+\delta}$ [7], and possibly by the observation of a weak magneto-optic Kerr effect rotation in zero external field [8], although no specific-heat anomaly has been reported. In order to search for a thermodynamic signature of this symmetry breaking, we have performed high precision measurements of the magnetic susceptibility in several underdoped and optimally doped YBa$_2$Cu$_3$O$_{x}$ (YBCO$x$) samples.

Measurements. – We have measured the magnetisation of sixteen YBCO polycrystalline$^1$ samples of various oxygen content. The different samples with their critical temperature $T_C$ whenever superconducting (determined for simplicity by the value of $T$ for which the magnetic susceptibility $\chi = 0$ at 1 tesla) are listed in table 1. The samples, of about typically $10^{-3}$ mol were prepared from three different batches at SPEC-CEA (Saclay, France), then compacted into right cylinders of 6 mm diameter and 6 mm height, and annealed under appropriate N$_2$-O$_2$ mixtures to obtain different oxygen contents, using a Netzsch thermobalance. Upon decreasing the oxygen concentration in the sample and therefore the carrier concentration, the $T_C$ of the superconducting samples was varied from 90.7 K down to 30.7 K, and three samples were made non-superconducting.

The samples were held in a long polyethylene straw of slightly smaller diameter and placed into a SQUID magnetometer, so that no sample holder correction was necessary. Their dc magnetisation was then measured using a 6 cm scan technique from below $T_C$ to 400 K, under a magnetic field of 1 T. In order to achieve the desired accuracy (besides choosing the maximum volume for the samples), the average of nine measurements was taken at each temperature with either 1 K or 2 K interval.

$^1$Typical size of the crystallites is about 30 $\mu$m.
Table 1: Summary of the results for different samples.

| Sample name | Oxygen content | $T_C$ (K) | $T_1$ (K) | $\chi_{300 \text{K}}$ (uncorr.) | $\frac{T d\chi}{dT}$ at $T_1$ | Batch # |
|-------------|----------------|-----------|-----------|-------------------------------|----------------------------|---------|
| YBCO6.19    | ±0.01          | ±1 K      |           |                               |                           | 3       |
| YBCO6.28    | 6.19           | -         | -         | 1.58                          | -                         | 3       |
| YBCO6.34    | 6.34           | -         | -         | 1.73                          | -                         | 3       |
| YBCO6.43    | 6.43           | 30.7      | 312 ± 2 K | 2.67                          | 0.31                      | 3       |
| YBCO6.47    | 6.47           | 45        | 317 ± 4 K | 2.61                          | 0.22                      | 1       |
| YBCO6.52    | 6.52           | 55.1      | 302 ± 2 K | 2.69                          | 0.27                      | 3       |
| YBCO6.53    | 6.53           | 57.5      | 315 ± 5 K | 2.69                          | 0.28                      | 2       |
| YBCO6.56    | 6.56           | 59.8      | 312 ± 2 K | 2.69                          | 0.26                      | 2       |
| YBCO6.60    | 6.60           | 60.8      | 238 ± 6 K | 3.11                          | 0.19                      | 1       |
| YBCO6.68    | 6.68           | 62.2      | 226 ± 2 K | 3.07                          | 0.18                      | 1       |
| YBCO6.73    | 6.73           | 67.5      | 212 ± 6 K | 3.30                          | 0.13                      | 1       |
| YBCO6.79    | 6.79           | 80.0      | 133 ± 15 K| 3.36                          | 0.15                      | 3       |
| YBCO6.90    | 6.90           | 90.9      |           | 3.56                          | -                         | 3       |
| YBCO7b1     | 7.00           | 90.7      |           | 3.95                          | -                         | 1       |
| YBCO7b2     | 7.00           | 90.7      |           | 3.94                          | -                         | 2       |
| YBCO7b3     | 7.00           | 90.6      |           | 3.81                          | -                         | 3       |

steps² In general, the reproducibility over 5 to 10 runs of the magnetisation measurements over warming or cooling could reach $10^{-7}$ emu or equivalently $10^{-8}$ $\mu_B$ per copper atom; however some constant shift of the magnetisation (of about $10^{-6}$ emu) of unknown origin occurred at times, without affecting the temperature derivative of the magnetisation, on which we focus in this work.

Experimental results. – The susceptibilities are shown in fig. 1 for a selected set of samples. For the nearly optimally doped samples ($x = 7.00$), the susceptibility above $T_C$ is almost constant in temperature, evocative of a Pauli contribution. However, a small Curie contribution attributable to parasitic phases is present, which we will discuss later.

As shown in fig. 1 the underdoped non-superconducting samples exhibit a susceptibility first decreasing with temperature, corresponding to a Curie contribution and then increasing at high temperature.

All the underdoped superconducting samples exhibit a negative susceptibility increasing at very low temperature, corresponding to the diamagnetism of the superconducting state, then decreasing due to some Curie contribution and then increasing again at high temperatures. The Curie term is found to vary slightly from batch to batch and to increase with underdoping. It is consistent with early observation from Johnston and co-workers [9,10], where it is ascribed to the presence of free Cu ions. The (uncorrected) susceptibility at 300 K decreases with decreasing oxygen content, due to the loss of carriers (see the inset of fig. 1) [9,10].

![Fig. 1: (Colour on-line) Susceptibility measured under 1T as a function of temperature for a set of samples. Inset: susceptibility measured at 300K at 1T as a function of oxygen content x. The samples are listed in the legend from top to bottom by decreasing value of the room temperature susceptibility.](image)

²A special check was performed on a $x = 7.00$ disc in order to measure the thermal diffusivity within the sample using the photothermal “mirage effect”. This yielded a time constant of less than 10s for our samples, compatible with the average rate of warming of $6 \cdot 10^{-3}$ K·s⁻¹.
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For the non-superconducting samples (YBCO6.19, YBCO6.28 and YBCO6.34), the derivative of the susceptibility continuously increases with no singular point in our range of temperature. (See, for example, samples YBCO6.19 and YBCO 6.28 in fig. 2.) However, we discovered a singular point in the derivative of the susceptibility in every underdoped superconducting sample (for 6.43 < x < 6.79) at a given temperature $T_1(x)$, x being the oxygen content. This is illustrated in fig. 3 for sample YBCO6.43, YBCO6.52, YBCO6.68 and YBCO6.79. The arrows indicate the position of $T_1$. Notice that all the derivatives merge above $T_1$.

This singular point consists in a change in the slope of the susceptibility at $T_1$ which is well visible on the susceptibility of the more underdoped samples as, for example, YBCO6.43 at about 312 K ± 2 K (see fig. 5a and inset). This translates into a downward step in the derivative of the susceptibility, whose height is found to be of the order of $10^{-3} \text{mm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ (see fig. 5b).

For less underdoped samples, the feature is somewhat less sharp but the anomaly is still well visible in the derivative. We choose, as a criterion for $T_1$, the onset temperature at which the derivative of the susceptibility starts decreasing yielding a cusp-like feature. $T_1$ is indicated by the arrows in figs. 3 and 5. The combination of the upward trend of the Curie term and the downward trend of the normal state susceptibility produces an inflexion point in the magnetisation, yielding a wide maximum in the derivative $\frac{dM}{dT}$. $T_1$ does not correspond necessarily to the position of this maximum which is strongly sensitive to the amplitude of the Curie term. (See for example sample 6.52 in fig. 3.)

It may happen that the cusp and the maximum coincide.
as in sample YBCO 6.68 (see fig. 3). At temperatures larger than $T_1$, for all the underdoped samples, the susceptibilities vary slowly with a similar slope, up to our maximum temperature of 400 K. The susceptibilities of the four nearly optimally doped samples YBCO7b1, YBCO7b2, YBCO7b3 ($x = 7.00$) and YBCO6.90 do not exhibit such a singular point at least within our level of accuracy ($\pm 10^{-7}$ emu \cdot K$^{-1}$). (See sample YBCO7b2 in fig. 4.)

Analysis and discussion. – In view of the small size of this effect, it is essential to check that this singular point is not related to the presence of parasitic phases at small concentration that are always present. The $Y_2BaCuO_5$ “green phase” was therefore checked quantitatively with EPR identification. This yielded a level of about only 0.1% mole, which is not consistent with the amplitude of the Curie term found in the optimally doped samples. This Curie term is indeed consistent with the presence of a few parts per thousands of $BaCuO_2$ (namely $Ba_{48}Cu_{48}O_{96}$) for which the apparent ferromagnetic Weiss temperature is of $+40$ K in the range $150-300$ K, as observed here and whose susceptibility is known to be featureless in this range [11]. The presence of CuO was checked by XRD to be less than 1%, thus making impossible for us the detection of the slope discontinuity of the susceptibility at $T_{CuO}^{N} = 230$ K [12]. A special run carried out on a pure CuO sample that had received the same oxygen treatment as the one necessary to make an underdoped YBCO sample with $x = 6.43$ did not show any measurable change of $T_{CuO}^{N}$. Therefore none of these well-characterised phases can account for the anomalies in the derivative of the susceptibility at $T_1$ (see footnote 3).

One may wonder whether this temperature $T_1$ could be associated with some oxygen ordering transition temperature. The only known transition occurring in this region of the phase diagram is the $O_1/O_{11}$ transition. Actually, this transition is known to take place at a much higher temperature, even for samples around $x = 6.5$ (where it is around 380 K), as may be seen in fig. 5 of [13]. However, in a very careful study, Liang and co-workers [14] have shown that the electron doping in the CuO planes $p$ is influenced by the order in the chains. Although we do not know the nature of the staggered magnetic order seen by neutrons, this order is most certainly related to $p$. Since the measurements are performed up to 400 K, where the oxygen is known to be mobile in the chains, it is therefore possible that for a given oxygen content $x$, the electron doping $p$ may vary and affect any quantity related to the electronic properties of the CuO planes. Therefore $T_1$ should be related to $p$.

Finally, systematic measurements of the magnetisation as a function of field in the full range of field and temperature available yielded an overwhelming linear field dependance superimposed over a small S-shaped hysteresis cycle saturating above 2 kgauss. This cycle, observed in all batches has a width of 300 gauss at 150 K and its saturation magnetisation decreases by 10% between 300 K and 400 K. The amplitude of the magnetic moment associated to this cycle, for which we have no definite interpretation, is about $10^{-2}$ emu \cdot mol$^{-1}$. Such cycles were previously reported [15] but the variation in the magnetic moment amplitude observed from batch to batch rules out any intrinsic origin. More recently, Xia et al. [8] have observed through polar Kerr effect measurements a rotation of the polarisation of light attributed to a magnetic moment below a temperature $T_S$. We have performed the same field training procedure as the authors of ref. [8]. We observe on sample YBCO6.60 a difference of magnetisation measured under 100 gauss between the $+3T$ and the $-3T$ preparation of about $10^{-7} \mu_B/Cu$. This difference of magnetisation is observed to be temperature independent between 100 K and 300 K at better than $10^{-8} \mu_B/Cu$. In similar samples, Xia et al. [8] find $T_S \sim 160$ K, which means that their signal corresponds to a magnetisation of less than $10^{-8} \mu_B$ per YBCO copper atom, in order to be consistent with our data.

The temperature $T_1$ is plotted in fig. 6 (blue down triangles) as well as $T_C$ (red dots) and the temperatures $T_{mag}$ obtained by Fauqué and co-workers [5] (green dots)

\footnote{It was also observed, for all the samples issued from batch 3, that at low magnetic field a well-defined, irreversible in temperature, magnetisation step-like feature of variable amplitude (typically $10^{-6}$ emu) occurred at 338 K. This very small contribution is attributed to the presence of a hitherto unspecified magnetic phase extrinsic to YBCO. Since only batch 3 is concerned, this phase cannot be responsible for the anomalies at $T_1$.}
and by Mook and co-workers [6] (blue square). As we pointed out earlier, it would be more appropriate to relate \( T_1 \) to \( p \) rather than \( x \), but we do not have any precise measurement of \( p \). \( T_1 \) is found to increase with underdoping and shows a remarkable agreement with \( T_{\text{mag}} \). This seems to establish a relationship between the anomalous character of the thermodynamic quantity \( \frac{dx}{dT} \) and the symmetry breaking evidenced by polarised neutron experiments.

In order to establish a relationship between the uniform magnetisation measured in this experiment and the staggered magnetisation evidenced by Fauqué [5], one way is to assume that the staggered magnetisation is coupled in second order to the uniform magnetisation in a way similar to that of an antiferromagnet. A mean-field calculation [16] then gives an estimate for the quantity \( \frac{dT_1}{dx} \sim 1 \) just below \( T_1 \) in the presence of staggered magnetisation. The corresponding value measured in the experiments is typically 0.15–0.3 in dimensionless units (see table 1), which we consider as a rather satisfactory agreement in view of the fact that the contribution of the (uncorrected) Curie-like terms gives a negative value for this quantity.

No evidence for a discontinuity in the specific heat in the underdoped regime of YBCO has been reported to date in the literature; however the observed magnetic moments [5,6] are of the order 0.1 \( \mu_B \)/Cu, which should lead to a sizeable change of entropy. In this respect, one should note that in the case of the antiferromagnetic transition of La\(_2\)CuO\(_4\) at 240 K, Sun et al. [17] have found no evidence for a specific anomaly at the transition in spite of a spectacular increase of the susceptibility, due to the very weak entropy variation involved in the 3D spin ordering. A more fundamental explanation might be that the staggered magnetic moments evidenced by Fauqué and co-workers [5] are predicted to be described by an Ashkin-Teller model [16,18–20]. For a range of parameters in such a model, the specific heat is not expected to have any singular behaviour, although the susceptibility to an external magnetic field is singular [18]. Since our present work is based on ceramic samples, a search for the corresponding (and possibly anisotropic) susceptibility anomalies in single crystals appears as a further test of these results.

**Conclusion.** – The present evidence of an apparently non-analytic variation of the temperature derivative of the susceptibility of YBCO within the pseudogap temperature range appears in direct contradiction with an essentially “featureless” crossover regime predicted by several models [1]. The overall agreement for the temperature of this susceptibility anomaly with that of the onset of staggered magnetisation points out toward a phase transition whose order parameter is weakly coupled to the external magnetic field.

We gratefully thank the following persons for stimulating discussions or experimental collaboration: V. Aji, J. Biscaras, P. Bourges, B. Fauqué, D. Fournier, A. Kapitulnik, W. Rischau, A. Shekhter, C. Simon and C. M. Varma.

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For the crystals used in ref. [8], the signal would be about two orders of magnitude smaller than in our samples, therefore below the noise level of our system. On the other hand, large single crystals usually contain a substantial amount of green phase producing a strong Curie term and thus making the observation of such small effects difficult.
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