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Coexistence of superconductivity \((T_c = 55 \text{ K})\) and antiferromagnetism \((T_N = 230 \text{ K})\) in \(\text{YBa}_2\text{Cu}_3\text{O}_{6.55}\) single crystal

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Résumé. Nous montrons par des études de diffusion de neutrons et de susceptibilité sur un monocristal de \(\text{YBa}_2\text{Cu}_3\text{O}_{6.55}\) qu’un ordre antiferromagnétique à longue distance coexiste avec la supraconductivité. La teneur en oxygène a été mesurée à partir de la détermination complète de la structure par diffraction de neutrons. Des mesures d’aimantation nous ont permis de mettre en évidence la supraconductivité en dessous de \(T_c = 55 \text{ K}\). La diffusion de Bragg magnétique a été observée jusqu’à \(T_N = 230 \text{ K}\) à la fois dans la phase supraconductrice et dans la phase normale.

Abstract. Neutron scattering and susceptibility measurements on a \(\text{YBa}_2\text{Cu}_3\text{O}_{6.55}\) single crystal show that the antiferromagnetic long range order coexists with superconductivity. The oxygen content has been determined by a complete neutron diffraction structure analysis. Evidence for superconductivity below \(T_c = 55 \text{ K}\) has been obtained from magnetization measurements. Magnetic Bragg scattering has been observed up to \(T_N = 230 \text{ K}\) in both the superconducting and the normal phase.

Introduction.

After the discovery of superconductivity with \(T_c \approx 90 \text{ K}\) in \(\text{YBa}_2\text{Cu}_3\text{O}_{6.9}\) [1], there has been great interest in the study of phonon-free mechanisms for superconductivity based on antiferromagnetic coupling between copper spins [2]. Antiferromagnetism in \(\text{YBa}_2\text{Cu}_3\text{O}_6\) has been first detected by muon spin rotation [3]

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More elaborated quantitative results concerning the magnetic structure and the electronic states have been obtained by neutron scattering experiments on single crystals [5].

It is now well established that the magnetic structure of YBa$_2$Cu$_3$O$_6$ consists of two planes of Cu(2) having the A.F. square lattice structure, which are antiferromagnetically stacked along the c-axis.

Since the motivation of investigating antiferromagnetism in Y-Ba-Cu-O compounds is mainly to settle whether it has some interplay, positive or negative, with superconductivity it is of crucial importance to study magnetic properties of YBa$_2$Cu$_3$O$_x$ as a function of the oxygen content x. From the first results obtained in the dependence of $T_N$ on x for $x < 6.5$, it has been inferred that antiferromagnetism should disappear at a concentration ($x = 6.3/6.4$) below the onset of superconductivity ($x = 6.5$) [3, 6].

We present here new results of magnetic neutron scattering on a single-crystal of YBa$_2$Cu$_3$O$_{6.55}$ which clearly reveal that the antiferromagnetic long range order is still present at an oxygen concentration where superconductivity is already observed.

Samples preparation and crystal structure determination.

Single crystals are prepared in a flux of BaCuO$_2$ and CuO between 1000 and 880°C in air, with a cooling rate of 0.4°C hour$^{-1}$, then slowly cooled down to room temperature in 20 hours. The crystals are extracted from a compact surrounding of flux. They exhibit irregular shape with generally only one well defined 001 face.

The composition of the crystal used for magnetic investigation, with volume $\approx 20$ mm$^3$, has been determined by a detailed structural analysis. The mosaic spread was evaluated on the (00l) reflections and corresponds to 0.45° (FWHM). The peak profile of (h00), (0l0) and (hkl) reflections (Fig. 1) revealed that the crystal exhibits the usual Y-Ba-Cu-O orthorhombic twinning. The data collection up to $2\theta = 80°$ ($\lambda = 0.8304$ Å) was performed at room temperature on the LLB 5C2 four circle diffractometer (scan range in $\omega$ up to 10° for integration of the two types of reflections resulting from the twinning). After averaging, the whole set of 435 independent reflections was kept for refinement, including the 32 reflections with $I < 3\sigma$. The procedure used for the refinement of orthorhombic twinned crystal is described in reference [8]: calculation of $F_{hkl} = \left[ (\alpha_1 F_{hkl})^2 + (\alpha_2 F_{hkl})^2 \right]^{1/2}$ and associated derivatives including expansion of Debye-Waller factor up to the 4th rank in tensors. The detailed results of several crystals, including this one, will be published elsewhere [9]. The final values for variable parameters are given in table I, and correspond to the formula YBa$_2$Cu$_{2.97(1)}$O$_{6.55(2)}$.

![Fig. 1.— Peak profile (ω-scan) of the 220 reflection which shows the orthorhombic twinning of the crystal.](image)

The outstanding feature of this result is that the additional $\alpha$ oxygen atoms in the formula YBa$_2$Cu$_{3-\alpha}$O$_{6+\alpha}$, $\alpha = 0.55 \pm 0.02$ in average, are all distributed on the O(4) site, whereas the occupancy of the O(5) site is strictly zero. As usual a slight copper deficiency is observed on the Cu(1) site.

Magnetic neutron scattering.

Magnetic neutron scattering experiments were performed on the 4F2 triple-axis spectrometer of the Orphée reactor in Saclay. A double graphite monochromator was used at $k_i = 2.66$ Å$^{-1}$ with a graphite filter placed in the incident beam in order to reduce the $2k_i$ contamination to $\sim 3 \times 10^{-4}$. Moreover because of the very low magnetic cross sections involved in this experiment we found it necessary to use a Ge(111) analyser to lower the contamination to $\sim 10^{-7}$.

The sample was mounted at the bottom of a close-cycle helium refrigerator for measurements between 10 K and 300 K.
Table I.- Structural parameters of the orthorhombic YBa$_2$Cu$_2$.97(1)O$_{6.55(2)}$ single crystal.

<table>
<thead>
<tr>
<th></th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$B_{equ}$</th>
<th>Occup.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>$1/2$</td>
<td>$1/2$</td>
<td>$1/2$</td>
<td>.35(1)</td>
<td>1</td>
</tr>
<tr>
<td>Ba</td>
<td>$1/2$</td>
<td>$1/2$</td>
<td>.1904(1)</td>
<td>.66(10)</td>
<td>2</td>
</tr>
<tr>
<td>Cu(1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>.76(10)</td>
<td>.97(1)</td>
</tr>
<tr>
<td>Cu(2)</td>
<td>0</td>
<td>0</td>
<td>.35828(5)</td>
<td>.38(1)</td>
<td>2</td>
</tr>
<tr>
<td>O(1)</td>
<td>0</td>
<td>0</td>
<td>.15555(8)</td>
<td>1.3(1)</td>
<td>2</td>
</tr>
<tr>
<td>O(2)</td>
<td>0</td>
<td>1/2</td>
<td>.3763(3)</td>
<td>.48(1)</td>
<td>2</td>
</tr>
<tr>
<td>O(3)</td>
<td>1/2</td>
<td>0</td>
<td>.3798(3)</td>
<td>.48(1)</td>
<td>2</td>
</tr>
<tr>
<td>O(4)</td>
<td>0</td>
<td>1/2</td>
<td>0</td>
<td>1.8(2)</td>
<td>.55(2)</td>
</tr>
<tr>
<td>O(5)</td>
<td>1/2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>.00(2)</td>
</tr>
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</table>

$a=b=3.857(3)$ Å, $c=11.728(11)$ Å. Final $R$ factor = 2.62% (2.40% for the 403 reflections with $l>3\sigma$), $wR = 1.02\%$. Twinning ratio $a_{2ki} = \frac{V_{2ki}}{V_{hkl} + V_{khl}} = 0.472(4)$.
The lattice constants are obtained from a routine reflection centering which underestimates the orthorhombic distortion because of partial overlap of $hkl$ and $khl$ reflections (see Fig. 1).

Figure 2 shows the two first magnetic reflections $(1/2,1/2,1)$ and $(1/2,1/2,2)$. The analysis of the magnetic intensities measured at $Q = (1/2,1/2,\ell)$ up to $\ell = 7$ and $Q(3/2,3/2,\ell)$ up to $\ell = 5$ leads to the same magnetic structure as previously determined for YBa$_2$Cu$_3$O$_6$ [5], namely antiferromagnetic ordering of the Cu(2) double layer and no ordered moment on Cu(1). However we measured a mean ordered moment of 0.12 $\mu_B$ on Cu(2) in this sample, a value much smaller than the $0.6 \mu_B$ determined for YBa$_2$Cu$_3$O$_6$.

Fig. 2.— Neutron scans in the $(h0h)$ direction across the two magnetic peaks $(1/2,1/2,1)$ and $(1/2,1/2,2)$ at $T = 15$ K and $T = 300$ K. solid lines are the profile corresponding to the resolution of the spectrometer.

Since no intensity has been found at $(1/2,1/2,\ell +1/2)$ points, there is no indication of a cell doubling as recently reported in a powder sample with $x = 6.35$ [10]. Besides no trace of satellite peaks have been observed around the $(1/2,1/2,\ell)$ peaks in the [110] and [001] directions, so that the possibility of a modulated structure, as observed for HoMo$_6$S$_8$ [11], can be ruled out.

The intensities of the peaks, which are weaker by a factor of 30 than the corresponding ones observed for YBa$_2$Cu$_3$O$_6$, correspond to scattering cross sections in the range 0.1 to 1 millibarn/steradian. Such a low scattering rate, of the order of $10^{-4}$ of the (006) nuclear peak, requires long counting times (3 to 6' per point) and a low background which can be obtained only with a 3-axis spectrometer and a single crystal sample.

The peak width is exactly given by the convolution of the resolution of the spectrometer with the mosaic distribution, which means that the spin correlation length is larger than 500 lattice units. The temperature dependence of the magnetic intensity at $(1/2,1/2,2)$ is shown on figure 3, from which we deduce $T_N = (230 \pm 5)$ K.

Magnetization measurements.

This crystal undergoes a superconductive transition at $T_c = 55$ K. Figure 4 shows a set of diamagnetic cycles at several temperatures. The 4.2 K isotherm exhibits a shape very similar to that of more oxygenated single crystals [12].
Fig. 3.— Intensity of the (1/2 1/2 2) magnetic reflection as a function of temperature.

Fig. 4.— Magnetisation versus field at various temperature for the YBa$_2$Cu$_{2.97(1)}$O$_{6.55(2)}$ single crystal. The magnetization drops rapidly with T (note the different M scales) and disappears at $T = 55$ K. The inset shows, at 4.2 K, the virgin branch near $H = 0$. It exhibits a bending above $H_{c1} \approx 15$ G. The direction of H with respect to the ab plane is $\approx 45^\circ$ and was imposed by the irregular shape of the sample.

Starting from $H = 0$ (after the sample has been cooled in zero field) and increasing the field we find that $M(H)$ is first linear with $H$ and reversible (to within less than 1 Oe) up to a threshold field of about 15 Oe. This field is identified as the first critical field $H_{c1}$ above which magnetic flux starts penetrating the bulk of the sample. As $H$ is further increased we observe an abrupt decrease of the slope leading to a sharp bending in the virgin curve (see inset on Fig. 4).

At much higher fields, the hysteresis displayed by the difference between ascending and descending branches of the high-$H$ cycle reveals that vortices are strongly pinned by local defects as in YBa$_2$Cu$_3$O$_7$ single crystals. Moreover, as for YBa$_2$Cu$_3$O$_7$ the $M(H)$ virgin branch does not saturate even at the highest available field for 35 kG. This, together with the absence of hysteresis at very low field (<15 Oe), indicates that the size of the current loops within the sample are of the same order (200 to 1000 µm) as for the fully oxygenated crystals [13]. It must be emphasized that sample inhomogeneities due to oxygen segregation would lead to a completely different behaviour of the granular type.

The above arguments strongly suggest that superconductivity in the present crystal is homogeneous on a scale extending at least from 100 Å to a few hundreds µm.

The critical temperature found for a crystal with this composition is in agreement with the results of Batlogg et al. [14], and is localized on the plateau of intermediate $T_c$.

Discussion.

Our results clearly demonstrate that antiferromagnetism and superconductivity coexist within the sample in YBa$_2$Cu$_{2.97}$O$_{6.55}$. Considering the effect of the oxygen content $x$ at low temperature one can say that a small antiferromagnetic long-range order can survive in a sample where superconductivity has already appeared. On the other hand, from the values obtained for $T_N$ (230 K) and $T_c$ (55 K), this also means that upon cooling, superconductivity appears at a temperature where antiferromagnetism has first established.

This new result [15] rises several questions. The first one is the apparent disagreement with previously reported results [6, 7, 16]. In the interpretation of their µSR experiments, Brewer et al. [7] came to the conclusion that antiferromagnetism should either disappear or be confined to very low temperatures for $x > 6.3$. However from our own neutron results as well as from
those of two other groups [6, 16], it appears that their results systematically lowers Neel temperatures for $x > 6.2$ and thus underestimates antiferromagnetism in such samples at a given temperature. This is probably because their $T_N$ is determined as the temperature at which half of the sample experiences a static local field. Obviously such a criterion would fail to detect such a weak antiferromagnetism as we have observed. The same argument of sensitivity probably also applies to neutron measurements on powder samples [16]. However, because our results also differ from single crystal measurements [6], one cannot disregard the possibility that magnetic properties can depend on an extra parameter such as the preparation and oxygenation conditions of the sample.

The second question is that of the chemical homogeneity of the sample specially concerning the oxygen content. To make sure that the observed coexistence does not result from a segregation within the sample between oxygen-poor and oxygen-rich regions of the crystal, we have made the following checks:

a) the first point is that around this concentration the $c$-parameter is strongly $x$-dependent so that oxygen concentration fluctuations should have given a broadening of the $(00\ell)$ peaks or in the case of segregation a doubling of the peaks. None of these effects have been observed,

b) the $(1/2 1/2 \ell)$ magnetic peaks have been found to be superimposed with the $r/2$ nuclear peaks observed by removing the $2k$ filters. This means that the $c$-parameters of the “AF crystal” coincide with that of the “mean crystal”,

c) in a sample containing several crystallites of different orientations, antiferromagnetism has been observed in all of them, d) the magnetic peaks were found to have resolution limited widths, so that antiferromagnetism cannot be confined in small oxygen-poor structural faults,

e) $T_N$, which is also $x$ dependent, is well defined and we have observed no rounding of the transition caused by $x$ fluctuations,

f) the value of $T_c = 55$ K corresponds to that previously reported for this composition [14]. A segregation would have led to the observation of superconductivity at higher temperatures.

A third question concerns the scale at which superconductivity and antiferromagnetism coexist. The simplest hypothesis is that of a fully homogeneous phase with both AF and SC. An alternative possibility is that a state with competing tendencies to AF and SC spontaneously splits into AF and SC domains. Though our results do not show any evidence for such a phase separation, this possibility cannot be completely ruled out. However the long-range AF order together with the strong bulk superconductivity reported here would impose strong restrictions on the size and the topology of such domains.

Conclusion.

Though the above arguments do not cover all possible cases, we think that they give strong indications that AF and SC do not appear in distinct regions of the sample with different oxygen concentrations but really coexists, which shed a new light on the problem of the interference of AF and SC. Further experiments are in progress to clarify the question.

References


[15] An experiment suggesting that magnetism could be present in a sample with $x = 6.59$ has been reported by MEZEI, F., FARAGÓ, B., PAPPAS, C., HUTIRAY, Gy., ROSTA, L. and MIHALY, L., Int. Conf. on High Temperature Superconductors, Interlaken, February 29, 1988, *Physica C* 153-155 (1988) 1669. However in this case only a disordered magnetic state was detected.