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CRITICAL FIELD OF SINGLE CRYSTALLINE $YBa_2Cu_3O_{7-\delta}$

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Good electrical contacts with a surface resistance $\lesssim 10^{-4}\,\Omega\,cm^2$ between gold wires and $YBa_2Cu_3O_{7-\delta}$ single crystals were made with an ultrasonic wedge bonder. From resisitivity measurements it is found that the dependence of T_c upon the magnetic field is highly anisotropic. With magnetic field $\boldsymbol{B} \| c$ a dramatic broadening of the transition is observed. This is interpreted as being due to disorder in the crystallographic (a, b) plane. The measured critical fields, extrapolated to zero temperature using the Werthamer, Helfand and Hohenberg formalism, are $B_{2c}^{\perp} = 23 \pm 1$ T and $B_{2c}^{\perp} = 180 \pm 10$ T.

1. Introduction

Since the discovery of high-T_c superconductivity [1] and the study of the sintered material by a number of groups it has become increasingly clear that the study of single crystals [2–8] is necessary for a better understanding of this exciting class of materials. In this context the smallness of the crystals presently available asks for a small contact area in resistivity measurements. Although resistivity measurements on single crystals were realized [3,5,9–12] previously, until now only a few reports [5] have appeared of samples with a sharp superconductivity transition above 90 K. The crystal used in this work has a T_c of 90.7 K and a transition width as determined from resistivity of less than 1 K. Using ultrasonic bonding we were able to make sufficiently small contacts to leave a large portion of the crystal that is sampled in our four point resistivity measurement.

2. Crystal preparation

Single crystals of $YBa_2Cu_3O_{7-\delta}$ were grown from the off-stochiometric composition (Y:Ba:Cu = 1:4:8.5) by partial melting followed by slowly cooling of the uncompacted, mixed, powder components. Crystals could the taken from the resulting matrix by picking them up with an ordinary tweezer. Typical crystal dimensions were $1 \times 1 \times 0.3$ mm^3. The crystals turned out to a superconducting without additional oxyen annealing. Details of the crystal growth procedure will be given elsewhere [13]. Using X-ray diffraction we established that the single crystals had their c-axis perpendicular to the largest face of the samples. The experiments described here were done on a single crystal of dimensions $0.57 \times 0.42 \times 0.18$ mm^3 (0.18 mm in the c-axis direction).

3. Bonding technique

Various techniques have been described to make electrical contacts on $YBa_2Cu_3O_{7-\delta}$ samples. Several of these are listed below. If specified by the original autors we show the contact resistance or resistivity in parentheses:

(i) Forced contacts i.e. pressing electrical contacts onto a crystal [14,15] (2–4 Ω).
(ii) Gold paint [2] (10 Ω).
(iii) Silver paint [3,16].
(iv) Copper pads evaporated onto the sample [12].

(v) Silver pads annealed with the sample at 900°C [17].
(vi) Gold pads annealed with the sample at 1065°C [18] (180 μΩ cm^2).
(vii) Indium solder [19].

Except for the forced contacts method, which is not appropriate for the relatively fragile single crystals, all methods lead to rather large contact surfaces.

Within the context of an ongoing program of resistometric studies of superconductors under very high pressures in our laboratory and in view of investigations of high-T_c superconductors in a diamond anvil cell [20–24] we devised a simple method enabling us to make contacts on small single crystals of typical dimensions $0.4\times0.4\times0.2$ mm^3. This technique is ultrasonic bonding.

We used a TU-907 Ultrasonic Wedge Bonder with a 10 G Controller, both from Mech. El. Industries (Woburn, MA, USA). Prior to the bonding the sample was glued onto a small piece of printed circuit board, with a soluble hard resin. No pre-treatment of the crystal surface proved to be necessary for the bonding. Contacts were made between the printed circuit board and the sample with 25 μm diameter beta-gold wires (that is gold with $\sim10^{-5}$ parts beryllium). Best results for the $YBa_2Cu_3O_{7-\delta}$ single crystals were obtained with the following bonding conditions. The sample was kept at room temperature. The bonding time was 60 ms, the power 1.5 W and the ultrasonic frequency 63 kHz. The force between the tip of the bonding machine and the sample was 29 gramforce. The conditions mentioned so far do not seem to be very critical.

Somewhat more critical is the temperature of the tip. Since the tip is rather small and the heating element is 2 cm away from the tip the result of the measurement of tip temperature depends on the experimental procedure. For this reason we describe the setup used by us to measure the temperature of the tip (see fig. 1). In place of the $YBa_2Cu_3O_{7-\delta}$ crystal a microscope cover glass (C) of thickness 0.15 mm is used. This is unsupported over a distance of 5 mm and rests on the sample holder (H) of the bonding apparatus. On the coverglass a copper constantan thermocouple (T) is placed (diameter copper wire: 80 μm, constantan wire 120 μm). The tip is pressed onto the thermocouple (T) with the bonding force (29 gf) and the thermovoltage is measured

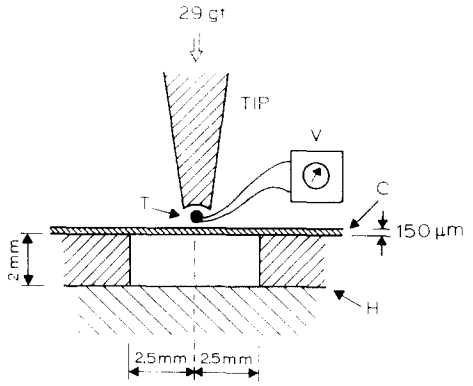

Fig. 1. The setup used to determine the tip temperature of the bonding apparatus. The tip is pressed with a force of 29 gramforce on the thermocouple T, which rests on a microscope cover glass C (0.15 mm thickness). Temperature is found from the thermovoltage as measured on voltmeter V. H is the standard sample holder of the bonding apparatus.

on a voltmeter V. From this measurement we obtained a tip temperature of 378 ± 15 K.

For the data presented herein, all 4 contacts were located on the same (001) face of the crystal. With different bonding conditions (30 ms, 0.75 W) it also proved possible to make contacts on the (100) or (010) faces. A typical contact resistance was $\sim$ Ω at 293 and ~3 Ω at 77 K. If after the first bonding the resistance was not satisfactory, good contacts could be made by bonding a fresh gold wire at the same spot. Since the contact area is certainly less than 40×100 μm^2, the surface resistance of the contacts is smaller than 10^{-4} Ω cm^2. Attempts were also made with aluminium wires (99% Al, 1% Si). This led to mechanically stronger contacts. The contact resistance, however, was $\sim10^2$ Ω at room temperature and increased to $\sim10^3$ Ω at 77 K.

4. Experimental procedure

The resistance of the sample was measured with a 4 probe dc technique. In order to eliminate the effect of thermovoltage induced in the contacts and/or other connections the current direction was reversed every 0.25 seconds and the amplitude of the measured voltage averaged. The current used was 1 mA. It was verified at zero magnetic field that the same results were obtained with a current of 100 μA. The

direction of the current was always parallel to the largest dimension of the crystal. The temperature was measured with a standard platinum resistor [$R(273\ \mathrm{K}) = 100\ \Omega$], calibrated in magnetic fields up to 5 T. In a typical experiment we kept the orientation of the crystal fixed and the magnetic field constant. The temperature was varied slowly (~ 0.1 K/min) and the voltage was plotted directly versus temperature. The curves shown in figs. 2 and 3 are not a fit to measured points, but are the original measurements.

5. Results

In zero magnetic field the resistivity has a linear temperature dependence from room temperature down to 120 K, extrapolating to a finite positive resistance at zero temperature. In figs. 2 and 3 the resistivity close to T_c is shown with the magnetic field $\boldsymbol{B}$ perpendicular ($\boldsymbol{B} \perp \boldsymbol{c}$), respectively parallel ($\boldsymbol{B} \parallel \boldsymbol{c}$) to the $\boldsymbol{c}$-axis of the crystal. Note that $T_c = 90.7$ K and the transition width of less than 1 K in zero field which is significantly sharper than reported in the literature [3,9,11,12]. We believe this is an indication of the good quality of the crystal. For $\boldsymbol{B} \perp \boldsymbol{c}$ (in fact $\boldsymbol{B}$ was parallel to the 0.42 mm edge of the sample) the width of the transition increases slightly with increasing magnetic field (fig. 2): the transition stays relatively sharp up to our highest fields. With the magnetic field parallel to the c-axis however there is a dramatic broadening of the transition (fig. 3).

Using the van der Pauw [25] technique the resistivity of the sample can be determined. This method is based on the assumption, that the current is distributed homogeneously along the thickness of the sample. Because of the reported [2] anisotropy in the conductivity this assumption probably is not valid. We nevertheless give the result: 10 mΩ in fig. 2 and 3 corresponds to a specific resistivity of 230 μΩ cm.

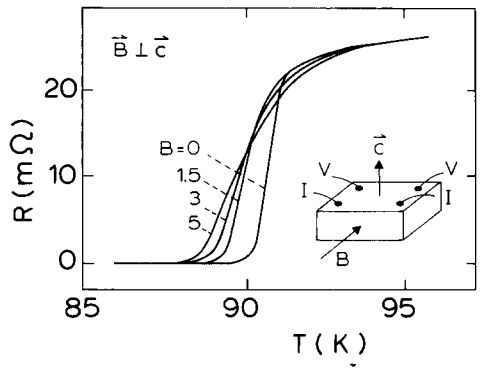

Fig. 2. Resistivity of $YBa_2Cu_3O_{7-\delta}$ as a function of temperature. Values for magnetic fields of 0, 1.5, 3 and 5 T are given. The magnetic field is perpendicular to the c-axis of the crystal.

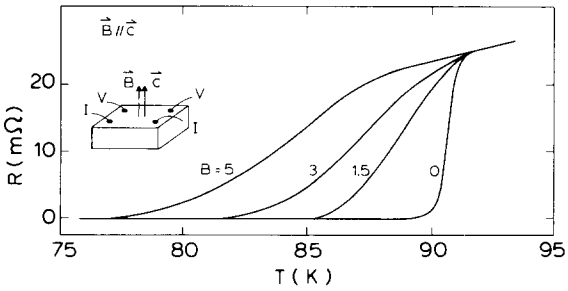

Fig. 3. Resistivity of $YBa_2Cu_3O_{7-\delta}$ as a function of temperature. Values for magnetic fields of 0, 1.5, 3 and 5 T are given. The magnetic field is parallel to the c-axis of the crystal.

Susceptibility measurements on crystals of the same batch were reported elsewhee by van den Berg et al. [26]. These give a T_c which is systematically lower than that observed resistivity. This has been tentatively attributed [27] to local enhancement of superconductivity at the twin planes.

Previously the broadening of the transition in *polycrystalline* samples was attributed to the random orientation of the crystallites [28]. To explain this width Welch et al. [28] postulated an anisotropy ratio $(\partial B_{c2}^{\perp}/\partial T)/(\partial B_{c2}^{\parallel}/\partial T)$ of 25 to 50.

However, at least the same amount of broadening of the transition with magnetic field is observed in single crystals with $\boldsymbol{B} \parallel \boldsymbol{c}$ (see e.g. fig. 3). We cannot completely rule out the possibility of inclusions of the flux from which our crystals were grown in our crystals. Since Laue photos gave no indication for their presence we assume them absent. Of course due to the twinning (which is present in our crystal) a randomness in crystal orientation with respect to the a- and b-axes is present. However, as $\boldsymbol{B}$ is perpendicular to the (a, b) plane we see from symmetry that, if the crystallites were independent of each other, this randomness cannot lead to a broadening of the transition. Therefore an other explanation is needed.

6. Discussion

A behaviour, similar to that observed by us has been predicted by Morgenstern et al. [29] for a square lattice of superconducting clusters with disorder. A cluster is a region of coherent phase and does not necessarily coincide with physical (sub) grain boundaries. The postulated two-dimensional spin-glass Hamiltonian is

$$H = -\sum_{i,j} K_{ij} \cos(\varphi_i - \varphi_j - A_{ij}) , \qquad (1)$$

where K_{ij} is the hopping matrix element of Cooper pairs from cluster i to a neighbouring cluster j, and φ_i is the phase of the wavefunction in cluster i. A_{ij} is a phase factor defined by

$$A_{ij} = \frac{2\pi}{\phi_0} \int_i^j \boldsymbol{A}\, \mathrm{d}\boldsymbol{l} , \qquad (2)$$

with ϕ_0 the flux quantum and $\boldsymbol{A}$ the vector potential of the magnetic field. In this model cluster-site disorder plays an essential role. From eq. (2) follows that this leads to a term proportional to $\boldsymbol{H}$ in Hamiltonian (1). Hence the width of the transition will increase with increasing magnetic field, as is observed (see figs. 2 and 3). At constant magnitude of the external field one expects the disorder to vary as $(\cos\theta)^2$ where θ is the angle between $\boldsymbol{H}$ and $\boldsymbol{c}$.

We now turn to the observed shift in T_c with applied magnetic field. Because the transition is broad one has to define T_c. A convention [28,30] has arisen to take for B_{c2} the temperature T_{cm} where the resistivity is half of the extrapolated normal state resistivity. However, in single crystals, where a mixture of components is not plausible, it seems to be more appropriate to take the zero resistance value T_{cf}. In the following we show T_{cf} as well as T_{cm}.

To summarize the experimental results we have plotted the critical field for both orientations $B_{c2\parallel}$ and $B_{c2\perp}$ versus temperature (fig. 4). In table I the slope of these curves is compared with the literature. For comparison with the result of Welch et al. [28] also the anisotropy ratio is shown. In comparing these results it must be noted that not all authors use the same definition of T_c, as indicated, and that several authors, notably Moodera et al. [12] report a clear curvature in $B_{c2}(T)$. Hence the value obtained for $\partial B_{c2}/\partial T$ is somewhat arbitrary. Also we observe that poorer quality samples would tend to have a smaller ratio $(\partial B_{c2}^{\perp}/\partial T)/(\partial B_{c2}^{\parallel}/\partial T)$. Using the Werthamer, Helfand and Hohenberg (WHH) theory [31] we have extrapolated our data to determine the criticalf field B_{c2} up to zero temperature. The results are plotted in fig. 5. The full curves refer to the zero resistance transition point T_{cf}. We also show (dashed curves) the behaviour of the T_{cm} transition point. The WHH

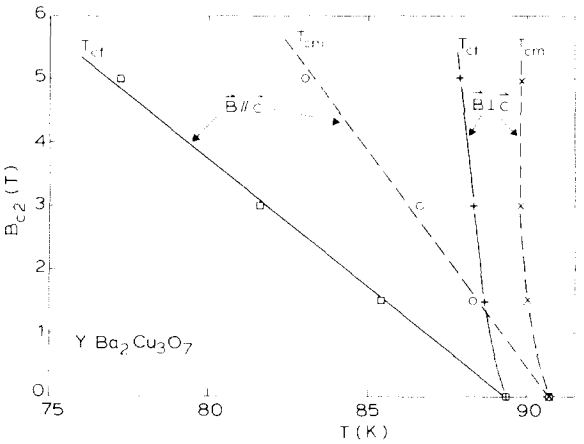

Fig. 4. Critical field B_{c2} versus temperature for the two orientations $\boldsymbol{B} \parallel \boldsymbol{c}$ and $\boldsymbol{B} \perp \boldsymbol{c}$. The dashed lines show T_{cm} (the temperature where the resistance has dropped by 50%). The full lines show T_{cf} (the temperature where the resistance is zero).

Table I
Slope of the temperature dependence of the upper critical field for the two field orientations $\boldsymbol{B} \perp \boldsymbol{c}$ and $\boldsymbol{B} \parallel \boldsymbol{c}$, and their ratio. The definition of critical field is indicated by T_{cm} (50% resistivity), T_{cf} (zero resistivity) and T_{co} (onset).

References	T_c	$\frac{\partial B_{c2}^{\perp}}{\partial T}$ (T/K)	$\frac{\partial B_{c2}^{\parallel}}{\partial T}$ (T/K)	$\frac{\partial B_{c2}^{\perp}/\partial T}{\partial B_{c2}^{\parallel}/\partial T}$ ratio
Resistivity measurements				
This work	T_{cm}	-6.0 ± 2.0	-0.7 ± 0.1	9
This work	T_{cf}	-3.5 ± 1.0	-0.4 ± 0.1	9
Hidaka et al. [3]	T_{cm}	-1.95	-0.37	5
Forro et al. [10]	T_{cm}	-3.1	-0.32	10
Moodera et al. [12]	T_{cm}	-3.6	-1.1	3
Magnetic measurements				
Worthington et al. [8]	T_{co}	-2.3	-0.71	3

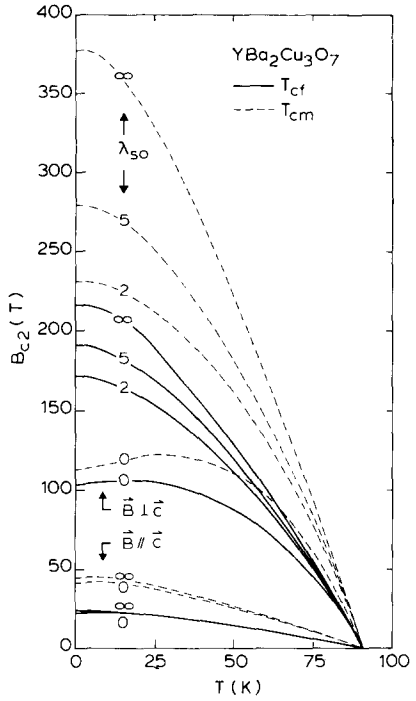

Fig. 5. Extrapolated critical fields B_{c2}. Lower curves apply to the orientation $\boldsymbol{B} \| \boldsymbol{c}$, upper curves to $\boldsymbol{B} \perp \boldsymbol{c}$. Full curves show T_{cf}, dashed curves T_{cm}. With each curve the corresponding spin–orbit coupling parameter λ_{so} is indicated.

parameter α was determined from the equation

$$\alpha = -0.52758 \left(\frac{\partial B_{c2}}{\partial T} \right)_{T=T_c} .$$

where $\partial B_{c2}/\partial T$ is to be expressed in tesla/kelvin [32]. Since the strength of the spin–orbit coupling is not a priori clear, the parameter λ_{so} is treated by us as unknown. For polycristalline $YBa_2Cu_3O_{7-\delta}$, van Bentum et al. [33] have proposed $\lambda_{so} \simeq 2$ by scaling the λ_{so} which best fitted measurements on $La_{1.85}Sr_{0.15}CuO_4$. For $\boldsymbol{B} \| \boldsymbol{c}$ we find the zero temperature critical field corresponding to T_{cf}: this is $B^{\|}_{c2f}(0) = 23 \pm 1$ T, independent of the exact value of λ_{so}. Also we see that the transition becomes very broad with a field $B^{\|}_{c2m}(0) \simeq 40$ T corresponding to T_{cm}. That is, if T_{cm} can be extrapolated in the same manner as T_{cf}. For $\boldsymbol{B} \perp \boldsymbol{c}$ we find $B^{\perp}_{2cf}(0) = 180 \pm 10$ T and $B^{\perp}_{2cm}(0) = 250 \pm 30$ T for $2 < \lambda_{so} < 5$ which seems a plausible regime [33]. These values exceed the Pauli limiting critical field [34] $H_P = 1.84 T_c = 170$ T.

7. Conclusions

Using ultrasonic bonding it is possible to do sensitive and accurate four-point resistivity measurements on very small (single) crystals.

Our partial melting method gives high quality single crystals. The broadening of the superconducting transition with magnetic field for $\boldsymbol{B} \| \boldsymbol{c}$ seems to be in agreement with a model disordered superconducting clusters.

From the field dependence of T_{cf} zero temperature critical fields $B^{\|}_{c2} = 23 \pm 1$ T and $B^{\perp}_{c2} = 180 \pm 10$ T were determined using standard WHH theory.

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