Polarized-neutron study of the $YBa_2Cu_3O_7$ system: Granular versus bulk superconductivity

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Neutron depolarization measurements have been carried out in order to investigate superconductivity in the $YBa_2Cu_3O_{7-x}$ system on both powdered and sintered polycrystalline samples. This technique provides indirect evidence of superconductivity through magnetic-flux trapping in low fields as well as vortex-line penetration in higher fields. Powdered and sintered samples show markedly different behavior, probably connected to their granular nature: a sintered sample traps magnetic flux by developing shielding currents when a low magnetic field (<100 Oe) is removed after being applied below the superconducting temperature T_c, whereas a powder does not. T_c can be well determined (about 90 K) whereas $H_{c1}(T)$ can only be estimated.

I. INTRODUCTION

Since the appearance of new high-T_c superconductors[1,2] about a year ago, numerous theoretical and experimental studies have been carried out in order to elucidate the nature and the origin of superconductivity in these copper-oxide-based ceramic materials. A crucial point is whether superconductivity is a bulk phenomenon, which has led to a revival of theories dealing with interactions between superconducting grains[3] as well as experiments comparing properties of sintered and powdered samples.[4]

A second important piece of physical information is the variation of the critical fields H_{c1} as a function of temperature. The reader is reminded of the early work of Weber[5] on conventional superconductors, in which H_{c1} was determined by use of polarized neutrons.

In this paper, we report on the first neutron depolarization measurements on both sintered and powdered $YBa_2Cu_3O_7$ polycrystalline samples and show that polarized neutrons constitute a useful tool to gain information on both points mentioned above.

II. EXPERIMENT

Preparation of the samples. The sintered $YBa_2Cu_3O_7$ sample is a cylinder of height 8.3 mm and diameter 13.2 mm. It was prepared from Y_2O_3, $BaCO_3$, and CuO at 950 °C in air. After several grindings and annealings, the resulting sample was pressed into pellets and sintered in an oxygen flux successively at 950 °C, 700 °C, and 500 °C, one day for each temperature and then slowly cooled down to room temperature in 5 h. The compactness coefficient was about 80%.

The powdered $YBa_2Cu_3O_7$ sample was pressed by hand into a cylinder made out of aluminum with a height and diameter of 10 and 12 mm, respectively. The thickness of the container was 0.13 mm. The powder was prepared starting from a mixture of Y_2O_3, $BaCO_3$ and CuO reacted around 900 °C in air. After several grindings and annealings, the powder was treated in an oxygen flux at 900 °C and slowly cooled down to room temperature. In both cases, x-ray powder diffraction revealed that the pure perovskitelike phase was obtained and the superconductivity was checked by magnetic field exclusion in liquid nitrogen.

Sample environment. The samples were placed in an Air Liquide Model RCF 304 closed-cycle cryogenic cooling system achieving effective temperatures down to about 16 K. Two collimating apertures were placed close to the sample position, one just before the cryogenic system and a finer one inside the cryogenic arrangement stuck onto the sample holder itself in order to prevent any spurious effect at low temperature due to the contraction of the inner stick that holds the sample. The sample holder was a vertical cylinder filled with helium gas to ensure good thermalization. The cylindrical samples were set so that their axes were parallel to the incoming neutron beam unless otherwise specified.

The spin-echo spectrometer[6] of the Laboratoire Léon Brillouin, located at the exit of a cold-neutron guide of the Orphée reactor was used for this study. The average incoming wavelength, defined to within 20% by a mechanical selector, was either 10.5 Å (highest polarization) or 7.3 Å (highest polarized flux). Magnetic fields could be applied using one of the following devices.

(i) The precession coils of the spin-echo machine, the stray field of which is parallel to the neutron beam and creates 7 Oe at the sample position. Inside these coils, the magnetic field B_0 is about 200 Oe. In the case of depolarization measurements, the aim of these stray fields was to avoid null field regions if necessary.

(ii) A Helmholtzlike coil assembly which can create horizontal magnetic fields as high as 440 Oe perpendicular to the neutron beam. In order to ensure that the neutron polarization follows adiabatically before entering and after exiting from the sample, the correction coil of the π flipper had to be set to a high enough current, creating a component of about 12 Oe parallel to the beam at the sample position. Such a current is required to avoid null field regions which could be created by the stray field of the Helmholtz coils along the neutron path.

One-dimensional polarization analysis.[7] In our geometry, the polarizer and the analyzer (both made of Fe-Ag supermirrors) are crossed due to the fact that one operates in transmission and the other in reflection. The neutron flux at the detector is then a minimum and not zero due to imperfections of our machine. This situation corresponds to the case where the polarization of the instrument itself is negative and very close to -1. Any depolarization or rotation of the beam polarization thus results in an increase of the counting rate. The usual procedure involving two flippers to reverse the neutron spins is used to obtain the net polarization of the outgoing neutron beam as well as the average depolarized counting rate and the efficiencies of both flippers as by-products. The average depolarized counting rate is proportional to the sample transmission and is used to check that a proper collimation is set at the sample: this rate should not vary as the temperature is lowered.

The absolute precision of our polarization measurements is typically about 0.01. All the figures quoted in this text are not corrected for the instrumental imperfect initial polarization.

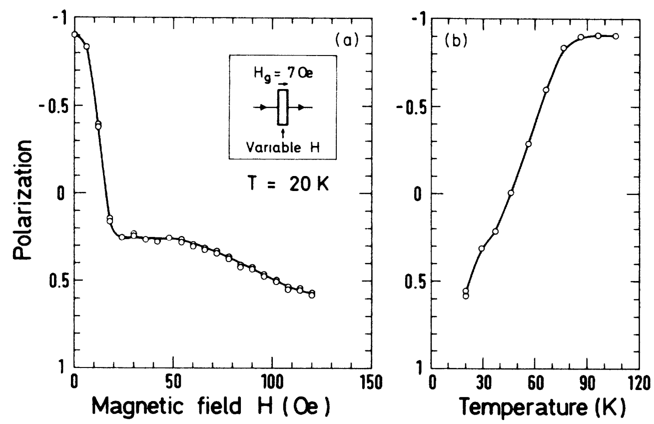

FIG. 1. (a) Polarization vs magnetic field H on sintered $YBa_2Cu_3O_7$ after cooling from 300 to 20 K. The polarization is measured after a given value of H has been successively switched on and then off. The final neutron polarization is not completely nil but is at least partially rotated. The neutron wavelength is 7.3 Å. H is the applied field normal to the neutron beam and H_g is a constant guide field parallel to the beam. Under the same conditions, a powdered $YBa_2Cu_3O_7$ sample did not alter the neutron beam polarization. The error bar related to the experimental data points is about the size of the symbols used to represent them. (b) Polarization vs temperature; once $H = 120$ Oe has been switched off on the sintered sample, the depolarization disappears at T_c (about 90 K).

III. RESULTS

Flux trapping in a low magnetic field. The samples were first cooled down to the lowest attainable temperature (about 20 K for our cryosystem) in a guide field H_g of about 7 Oe parallel to the neutron beam. No change of polarization was observed upon cooling, within the precision of our measurement (about 0.01). A magnetic field H perpendicular to the neutron beam was then applied using a Helmholtz-like pair of nonremanent coils, with the guide field H_g of about 7 Oe parallel to the neutron beam being still present. The field H was switched on and off for increasing values ranging from 0 to 120 Oe. The final neutron polarization was measured after H had been switched off (but not H_g) and before it had been switched on again with an increased value.

This procedure was first carried out on the sintered sample. In that case, a partial reversal of the polarization was observed: after the last value of H (120 Oe) was switched off, a positive polarization of about +0.60 was measured [Fig. 1(a)]. This observation indicates a nonadiabatic behavior of the neutron spin in the sample, which is an evidence of sharp changes of the magnetic field direction over very short distances. Moreover, the polarization was then found not to relax at least for one day. The original polarization was restored when the sample was heated up above T_c, which is about 90 K for our sample [Fig. 1(b)]. In order to observe the evolution of this phenomenon as a function of temperature, the following procedure was adopted. (i) The 7-Oe guide field was suppressed so that the remaining external field H (when applied) was purely normal to the neutron beam. (ii) The sample was heated up well above T_c and then zero-field-cooled down to about 20, 76, 86, and 91 K, respectively. The external field H was subsequently applied, then switched off, and the polarization measured using the same procedure as described above. The result is shown on Fig. 2(a). Indeed, the effect disappeared above T_c: the measured curve obtained at 91 K in Fig. 2(a) is almost flat. It was then checked that all the perturbations induced in the sintered sample when the highest value of H was switched off at the four temperatures mentioned

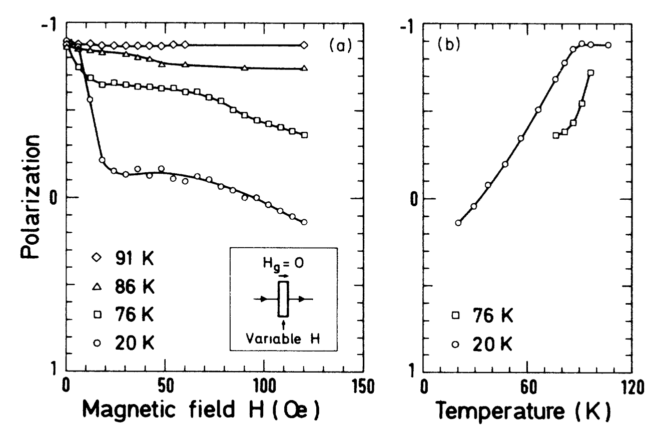

FIG. 2. Same as above (except for H_g), after cooling the sintered sample from 300 to 20, 76, 86, and 91 K, respectively. Neutron depolarization occurs only when the sample is cooled down below T_c. Due to the small temperature ranges involved, the repolarization curves corresponding to 86 and 91 K were not measured.

above disappeared upon heating the sample above T_c [Fig. 2(b)]. No such depolarization effects could be observed on the powdered sample up to 120 Oe.

We observed that a field of 20 Oe is enough to induce a huge effect on the final neutron polarization in the case of the sintered sample [Figs. 1(a) and 2(a)]. This value is much smaller than the estimation of roughly 500 Oe for H_{c1} given in Ref. 8. This result, together with the absence of any depolarization effect in the case of the much less dense powder lead us to the following possible explanation: due to the closer contact between the grains in the sintered sample, superconducting paired electrons can jump from one grain to another (possible weak links, see Ref. 9, Chap. 11). The apparently singly-connected sintered polycrystalline sample is effectively turned into a multiconnected superconductor where pairs of superconducting electrons can perform loops circling nonsuperconducting regions. Supercurrents can then be induced in the sample, much in the same way they are induced in a superconducting ring. An alternative explanation is that, for a given temperature, the internal magnetic field inside a granular superconductor can be much larger than the external applied one and hence than H_{c1}, due to the diamagnetic interactions between superconducting grains.[3]

Magnetic field pinning. In order to check for a possible pinning of the trapped flux, the procedure described in the above paragraph was carried out repeatedly at a temperature of about 20 K: after the highest magnetic field (120 Oe) has been switched off, the magnetic field was increased again progressively from zero. After observing first the partial reversal of the neutron polarization [Fig. 3(a)] all three subsequent cycles resulted in a constant value of the final neutral polarization independent of the magnetic field H being switched off [Fig. 3(b)] evidencing some pinning effect. The polarization was also measured before the field H was switched off, yielding the upper curves of Figs. 3(a) and 3(b). Due to the stray fields from the coils creating H, the guide field H_g was essential to prevent spurious depolarization due to the setup itself in the course of the measurements with the field H switched on. The latter were found to be reproductible [note the upper three superimposed curves on Fig. 3(b)] yielding polarization values which are very close to the maximum value of the polarization. The slight decrease between 60 and 120 Oe can result from a depolarization induced by our experimental setup but the similar falling trend of the lower curve (with H off) in Fig. 3(a) leads us to favor the hypothesis of grain penetration by superconducting vortices, all the more so that the same kind of experiments on the powder did not show any depolarizing effect. H_{c1} would then correspond to an applied external field of about 60 Oe at 20 K. The fact that no such effect could be observed on the powder can be reconciled with the H_{c1} hypothesis, if one accepts that the effective field acting on the powder grains is less than the one acting on the grains inside the sintered sample, due to a looser contact between them and hence to a weaker diamagnetic interaction following Waysand's explanation.[3]

Depolarization in a higher magnetic field. In order to observe a superconducting behavior of the powdered sample using neutrons, the external magnetic field range was extended up to 440 Oe by adding soft-iron pieces in our Helmholtz-like pair of coils. Unfortunately, the remanence of these pieces prevented us from studying the trapped flux in higher fields. On the other hand, it enabled us to carry out measurements with the field switched on. Both the powdered and the sintered samples were zero-field cooled down to about 20 K. The external field H was then applied continuously from 0 to 440 Oe.

For both the powdered and the sintered samples, the polarization started to decrease significantly for an applied external field of about 100 Oe. This may indicate the occurrence of the flux penetration inside individual grains since the value of the magnetic field H necessary to observe this effect is of the same order of magnitude for both samples [Figs. 4(a) and 4(b)]. The field value is only indicative since a guide field of about 12 Oe parallel to the beam had to be applied to prevent depolarization due to the stray fields of our Helmholtz-like coils. One further experimental difficulty was due to the stray fields from the

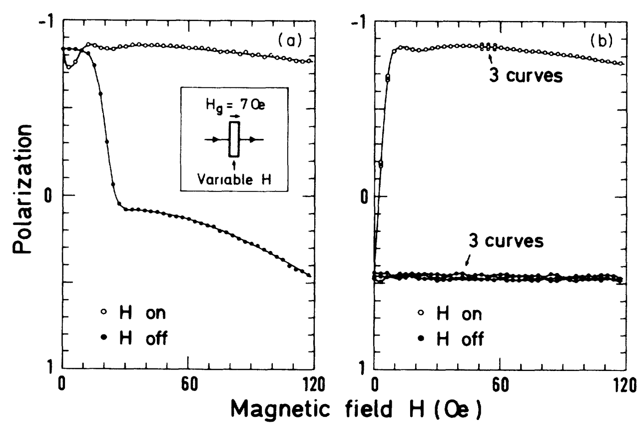

FIG. 3. (a) Polarization vs applied (O) and then removed (●) magnetic field H on the sintered sample at about 20 K. (b) The sequence in (a) is repeated three more times, yielding two sets of three superimposable curves.

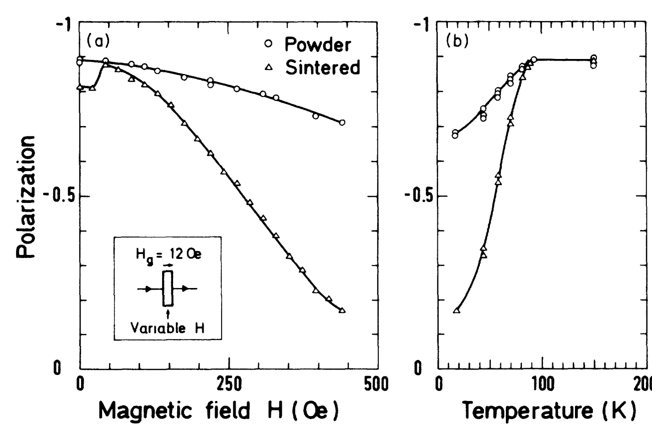

FIG. 4. (a) Polarization vs applied magnetic field H for both the powder (O) and the sintered (△) samples at about 20 K. (b) In both instances, neutron depolarization disappears at $T_c \simeq 90$ K, the magnetic field $H = 440$ Oe being continuously applied.

magnetized soft-iron pieces used to extend the magnetic field range: whether they were inserted in the Helmholtz coil pair before or after cooling resulted in spurious depolarization effects in fields less than 100 Oe. This effect is particularly significant on the curve pertaining to the sintered sample in Fig. 4(a). We checked that this effect was only present below T_c. That the experimental setup was not responsible for the depolarization occurring for higher field H values was checked in two ways. First, the same experiment above T_c did not depolarize the beam. Second, the depolarization effect disappeared when the temperature was raised from 20 K above T_c, the maximum field of 440 Oe still being applied [Fig. 4(b)]. That a neutron beam is (slightly) depolarized above H_{c1} has already been observed and discussed by Weber in standard superconductors.[5] Moreover, the following observation was made: at 20 K on the powder sample, after switching off the 440 Oe external field and taking off the remanent soft-iron pieces, the depolarization remained unchanged [about -0.70: see Fig. 4(a)] and did not relax, indicating a pinning of trapped flux lines in the powder.

IV. CONCLUSION

The role of the granular nature of our polycrystalline samples was evidenced by a systematic comparison between the powdered and the sintered $YBa_2Cu_3O_7$: the latter is able to trap magnetic flux below T_c in applied fields less than 20 Oe whereas the former, whose constitutive grains are in much looser contact, does not trap any flux up to 120 Oe. Moreover, the corresponding depolarizing effects become weaker as the temperature is raised toward T_c and disappear at T_c. High-pressure studies at low temperature in a nonmagnetic cell are suggested to extend our results concerning the effects of intergrain interactions in polycrystalline samples.

At the temperature of 20 K, both the powdered and the sintered samples significantly depolarize the neutron beam in applied magnetic fields above 100 Oe. This result has two implications. First, this is a bulk effect affecting individual grains. Second, neutron polarization measurements can be used to determine H_{c1} as a function of temperature. At 20 K, H_{c1} appears to be of the order of 100 Oe.

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[1]J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).
[2]M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 405 (1987).
[3]G. Waysand, Europhys. Lett. **5**, 77 (1988).
[4]D. X. Chen, R. B. Goldfarb, J. Nogues, and K. V. Rao, J. Appl. Phys. **63**, 980 (1988), and references therein.
[5]H. W. Weber, J. Low Temp. Phys. **17**, 49 (1974).
[6]R. J. Papoular, R. Millet, L. Rosta, and F. Mezei, Proceedings of the Workshop on Neutron Physics, Budapest, 1986 (unpublished).
[7]See, for instance, J. Hayter, in *Neutron Diffraction,* edited by H. Dachs, Topics in Current Physics, Vol. 6 (Springer-Verlag, New York, 1978) (most relevant is section 2.4.1).
[8]B. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and G. P. Espina, Phys. Rev. Lett. **58**, 1676 (1987).
[9]A. C. Rose-Innes and E. H. Rhoderick, *Introduction to Superconductivity,* 2nd ed. (Pergamon, New York, 1980), Chap. 2, p. 19.