Influence of Fe impurities on the Y-Ba-Cu-O superconducting system

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We have studied the influence of Fe impurities in high-temperature superconductors of the type $Y_{1.2}Ba_{0.8}CuO_{4-\delta}$ and $YBa_2Cu_3O_{7-\delta}$ on the critical temperature as measured by the resistance transition. The chemical compositions of the different phases have been determined using a scanning electron microscope and electron-probe microanalysis. We find that for low concentrations Fe substitutes for Cu in the superconducting phase. The transition temperature decreases linearly as a function of the Fe concentration, in remarkable analogy with the situation in conventional superconductors with paramagnetic impurities.

Since the very exciting discovery by Bednorz and Müller[1] of high-temperature superconductivity in copper oxides and the subsequent rush of many laboratories into this fascinating field,[2] the research has been directed to reaching even higher T_c's, to investigating the use of these new materials for technical applications, and to understanding the underlying mechanism. For this last goal, it is worthwhile to repeat the most significant classical experiments with conventional superconductors on these novel materials. In this spirit, it is the purpose of this present note to report on the effect of magnetic impurities (Fe) on the critical temperature T_c of the high-temperature superconducting system Y-Ba-Cu-O. Determinations of the transition temperature T_c by simple resistance measurements show a sharp linear decrease in T_c as a function of the Fe impurity concentration.

As has been seen in the pioneering experiments of Matthias, Suhl, and Corenzwit[3] and subsequently by many other later findings, the addition of paramagnetic impurities to the conventional superconductor results in a rapid linear decrease of its superconducting transition temperature T_c with increasing impurity concentration. It has been shown that the effect is due to exchange interaction between the paramagnetic impurities and the conduction electrons, rather than magnetic-dipole interaction, and the relevant theory was put on firm grounds by the seminal paper of Abrikosov and Gorkov.[4] Subsequent experiments by Reif and co-workers[5] confirmed this theory in detail, in particular the interesting fact of gapless superconductivity. All this and related work, obviously based on the Bardeen-Cooper-Schrieffer (BCS) theory, is described in Maki's[6] masterful review. In contrast to the case of nonmagnetic impurities, paramagnetic impurities give rise to real lifetime effects of the Cooper pairs. The Hamiltonian describing the interaction of the impurity spins with the electron spins is not invariant under a time-reversal transformation; this leads to the breaking of pairs formed from time-reversed states, and therefore to a reduction of the ordering parameter.

For this present study, we have made Y-Ba-Cu-O samples with the highest possible T_c, as recently described in the literature,[7,8] i.e., the multiphase polycrystalline system $Y_{1.2}Ba_{0.8}CuO_{4-\delta}$ (samples A) and the single-phase polycrystalline oxygen-deficient perovskite $YBa_2Cu_3O_{7-\delta}$ (samples B). As starting materials, we used fine dried powders of Y_2O_3, $BaCO_3$, CuO, and Fe_2O_3 as impurities. Powder mixtures of appropriate composition were well mixed, sintered in oxygen at 1100 °C for samples A and 900 °C for samples B during 3 h, cooled down in oxygen flow, pulverized, and then pressed into pellets with a thickness of about 1.5 and 13 mm in diameter. (Note that all samples investigated had approximately the same geometrical size.) Then the samples were sintered during 5 h in oxygen, again at 1100 °C for samples A and 900 °C for samples B. Finally, the samples were slowly cooled down, again in oxygen. Aluminal crucibles were used for the heating and annealing of all the samples.

After preparation, the samples were analyzed with respect to their chemical composition and structure with the help of a scanning electron microscope (SEM), type Jeol-JMS-35C, equipped with an energy-dispersive EDAX spectrometer. This electron-probe microanalysis (EPMA) allows a quantitative examination and analysis of the different components and different phases present in the samples. In this way, the main phases have been confirmed, together with minority phases, notably CuO. Figure 1(a) shows an example of a SEM image with back-scattered electrons of one of the samples (No. 3). Figure 1(b) shows the Y distribution of the same part as Fig. 1(a) using the Y *La* signal (EDAX); phases with different Y concentrations (superconducting and semiconducting) can clearly be distinguished. The needle-shaped crystals represent the superconducting phase, the circular crystals the semiconducting phase, and the black regions the CuO phase. The EPMA allows a determination of the concentration of the different elements forming a particular phase, including the magnetic impurities. Figure 2(a) shows the spectrum of the superconducting $YBa_2Cu_3O_{7-\delta}$ phase in sample No. 7; a significant amount of Fe is observed. A more quantitative analysis of the spectra indicates that Fe seems to substitute the Cu atoms. Figure 2(b) shows the spectrum of an EDAX microanalysis of

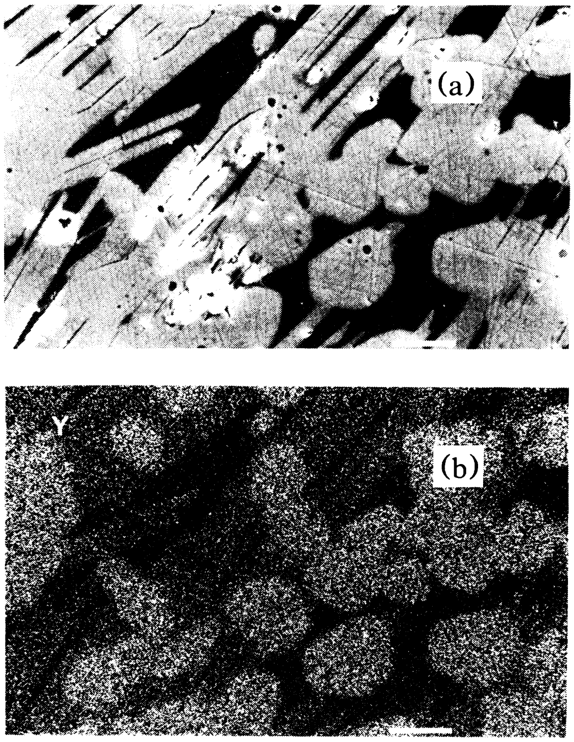

FIG. 1. Electron microscopy of sample No. 3. (a) Conventional image of back-scattered electrons by SEM. (b) Same part of the sample as (a), but using the Y $L\alpha$ signal to show the several phases with different Y concentration. Needle crystals: superconducting phase $YBa_2Cu_3O_{7-\delta}$ (less content of Y). Circular crystals: semiconducting phase Y_2BaCuO (more content of Y). Black regions: CuO phase (very small content of Y). (The horizontal white bar represents the length scale of 10 μm.)

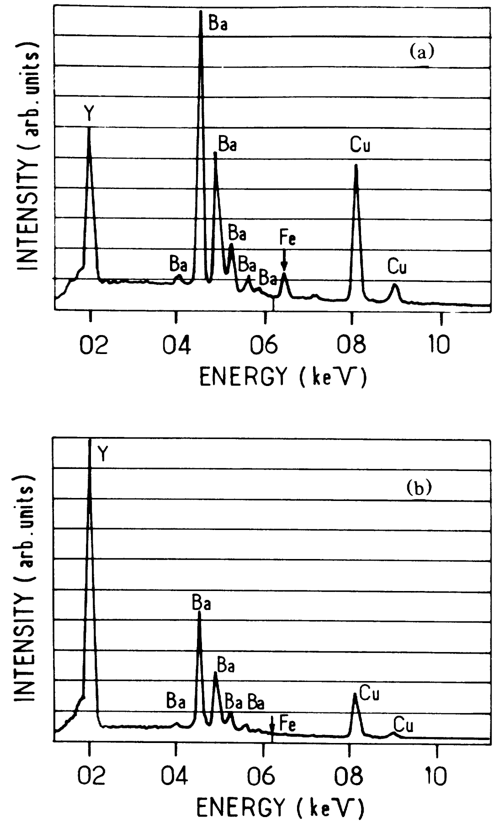

FIG. 2. EDAX microanalysis of sample No. 7. (a) Superconducting phase $YBa_2Cu_3O_{7-\delta}$. A significant amount of Fe is observed, in substitution for Cu. (b) Semiconducting phase Y_2BaCuO_5. No significant amount of Fe is observed.

the semiconducting Y_2BaCuO_5 phase in the same sample; note that despite the fact that a considerable portion of FeO_3 has been added in the preparation (1% of Fe in weight percent of Fe_2O_3 added), *no* significant amount of Fe is observed.

The superconducting transitions were determined by simple resistance measurements, using a four-probes method. The contacts were attached with silver paste. The currents were kept very low (50–500 μA) in order to avoid any disturbing effects as much as possible. The measurements have been carried out in a helium-flow cryostat (Oxford Instruments), the temperature was calibrated with a germanium resistor (Cryocal Florida). The room-temperature resistance of the samples was between 2.5 and 200 mΩ. Figure 3 shows the temperature dependence of the resistivity of all the samples investigated; the resistance of all the samples has been normalized to 1 at their highest values between 0 and 110 K.

The main findings of our study are collected in Table I. The results can be summarized as follows

(1) For low concentrations of Fe_2O_3 we always find two important phases present: The semiconducting phase Y_2BaCuO_5 and the superconducting phase $YBa_2Cu_3O_{7-\delta}$. This is in agreement with reported results from

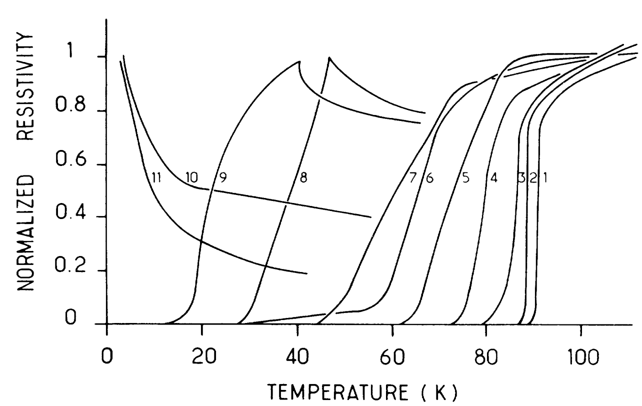

FIG. 3. Temperature dependence of the resistivity of the different samples. For illustrative purposes, all the curves have been normalized to their maximum value between 0 and 110 K (see Table I). For the different curves, the Fe composition in the superconducting phase (as determined by SEM and EPMA) and measured as the atomic ratio $c_{Fe/Cu}$ with respect to Cu is given, respectively, by 1, 0.024% multiphase (mp) $Y_{12}Ba_{0.8}CuO_{4-\delta}$; 2, 0.03% single phase (sp) $YBa_2Cu_3O_{7-\delta}$; 3, 2.55% (mp); 4, 2.82% (sp); 5, 5% (sp); 6, 10.1% (mp); 7, 10.7% (mp); 8, 11.4% (mp); 9, 11.3% (sp); 10, 13% (sp); 11, 13% (sp).

TABLE I. Summary of the relevant properties of the Y-Ba-Cu-O systems with and without Fe impurities, studied by resistivity measurements, SEM and EPMA.

Sample No.	Type of sample $Y_{1.2}Ba_{0.8}CuO_{4-\delta}$ (A, multiphase); $YBa_2Cu_3O_{7-\delta}$ (B, single-phase)	Fe impurity in wt.% of Fe_2O_3 added to initial composition (A or B) (%)	Superconducting phase $YBa_2Cu_3O_{7-\delta}$ (from SEM and EPMA)	Semiconducting phase Y_2BaCuO_5 (from SEM and EPMA)	New Phase $Y_1Ba_1Cu_1Fe_{1-\delta}O_5(\delta \simeq 0.2)$ (from SEM and EPMA)
1	A	0.03	Yes	Yes	No
2	B	0.03	Yes	No	No
3	A	0.24	Yes	Yes	No
4	B	1	Yes	No	No
5	B	2	Yes	No	No
6	A	2	Yes	Yes	Yes
7	A	1	Yes	Yes	No
8	A	4	Yes	Yes	Yes
9	B	4	Yes	No	Yes
10	B	6	Yes	No	Yes
11	B	8	Yes	No	Yes

Sample No.	Atomic ratio $c_{Fe/Cu}$ in superconducting phase (from SEM and EPMA) (%)	Atomic ratio $c_{Fe/Cu}$ in semiconducting phase Y_2BaCuO_5 (from SEM and EPMA) (%)	Other semiconducting phases	Critical temperature T_c at half-height (K)	Resistivity broadening (ΔT) in transition region (K)	Sample Resistivity at 100 K ($\pm$15%) (mΩcm)
1	0.024	0.006	No	92	2	48
2	0.03	0	No	89	2	2.47
3	2.55	0.17	No	86	6	1.80
4	2.82	0	No	80	10	5.76
5	5	0	Yes	74	24	7
6	10.1	0.7	No	64	10	163
7	10.7	0.8	No	60	30	264
8	11.4	1.7	No	36	10	226
9	11.3	0	Yes	20	10	28.8
10	13	0	Yes	0	0	48.2
11	13	0	Yes	0	0	120

samples without Fe impurities.[8] In this context, we would like to emphasize the fact, that in contrast to most other workers[2] we did not use ultrapure starting materials for the preparation of our samples [the impurity concentration of the starting materials was indicated by the supplier as Y_2O_3 (99.99%), $BaCO_3$ (99.2%), CuO (99%), and F_2O_3 (99%) for the impurities to add]. Nevertheless, the measured values for T_c of our samples without Fe_2O_3 was the same as reported for samples with ultrapure starting materials. This could be an indication of the fact that T_c for the Y-Ba-Cu-O system is, just as in the case of conventional superconductors, rather insensitive to most impurities.

(2) The EPMA shows that for low concentrations of Fe_2O_3 almost all the Fe can be found in the superconducting phase. A comparison between different samples indicates that by introducing the Fe into the superconducting phase, the Cu $K\alpha$ line intensity is reduced in favor of the Fe lines, while the intensities of the Y $L\alpha$ lines and the Ba $L\alpha$ lines stay constant. This seems to indicate that the Fe atoms substitute for the Cu atoms and is reasonable if the perovskite structure should be kept intact; the Y ions and the Ba ions are both bigger than the Fe ions, their replacement is, therefore, less probable.

(3) The superconducting transition temperature decreases linearly with the concentration of Fe (measured, e.g., as the atomic ratio $c_{Fe/Cu}$ of Fe vs Cu in the superconducting phase) for low concentrations of Fe (up to 12%) (Fig. 4). This could be explained on the basis of the Abrikosov-Gorkov theory,[4] and is in qualitative agreement with the experiments of Reif and co-workers[5] on films of In with Fe impurities (note the difference in slope of 2.8 K/$c_{\text{atom\% Fe/Cu}}$ for the Y-Ba-Cu-O system as compared with 2 K/$c_{\text{atom\% Fe/In}}$ for In films).

(4) Above a certain concentration of Fe_2O_3 in the initial composition, no more Fe seems to be getting into the superconducting phase and a saturation at an atomic ratio $c_{Fe/Cu}$ at 12% occurs. This is accompanied by the appearance of a new phase $Y_1Ba_1Cu_1Fe_{1-\delta}O_5$ ($\delta \simeq 0.2$). For these samples, the temperature dependence of the resistance in the normal state seems to change into a semiconducting behavior (Fig. 3, Table I). For these higher con-

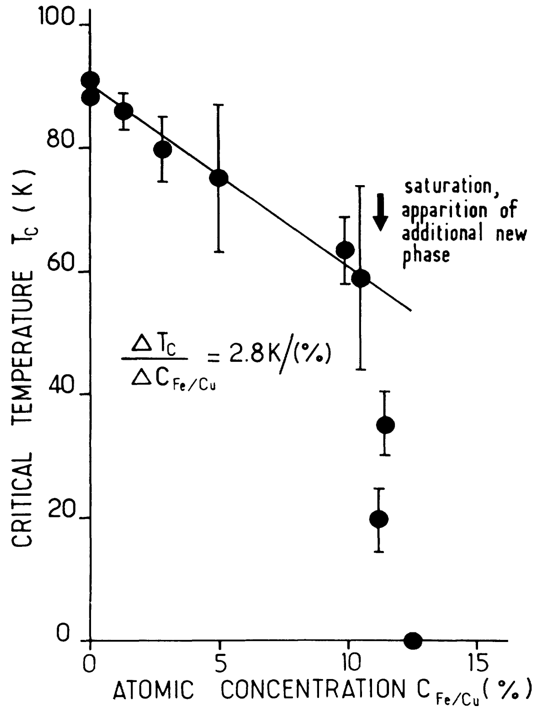

FIG. 4. Critical temperature T_c of the Y-Ba-Cu-O superconducting system as a function of Fe impurities, measured as the atomic ratio $c_{Fe/Cu}$ in the superconducting phase.

centrations of Fe_2O_3 in the starting composition, the T_c of the superconductor is drastically reduced down to 0, although the Fe concentration in the $YBa_2Cu_3O_{7-\delta}$ phase seems to stay constant. A possible mechanism to reduce superconductivity in these concentrated systems could be the proximity effect of the excess Fe in the nonsuperconducting phases, which are in very close contact with the superconducting parts.

In conclusion, we have shown experimentally that Fe as a magnetic impurity reduces the critical temperature T_c of the high-temperature superconductor Y-Ba-Cu-O. For low Fe concentrations, T_c decreases linearly with the impurity concentration. We believe that these kinds of experiments have some significance for the theory[9] of these novel high-T_c superconductors: A not-time-reversal-invariant interaction seems to be able to reduce (or even destroy) superconductivity. The Abrikosov-Gorkov extension of the BCS theory is able to explain these experimental findings remarkably well. However, very obviously more detailed microscopic experiments are needed to clarify these problems.

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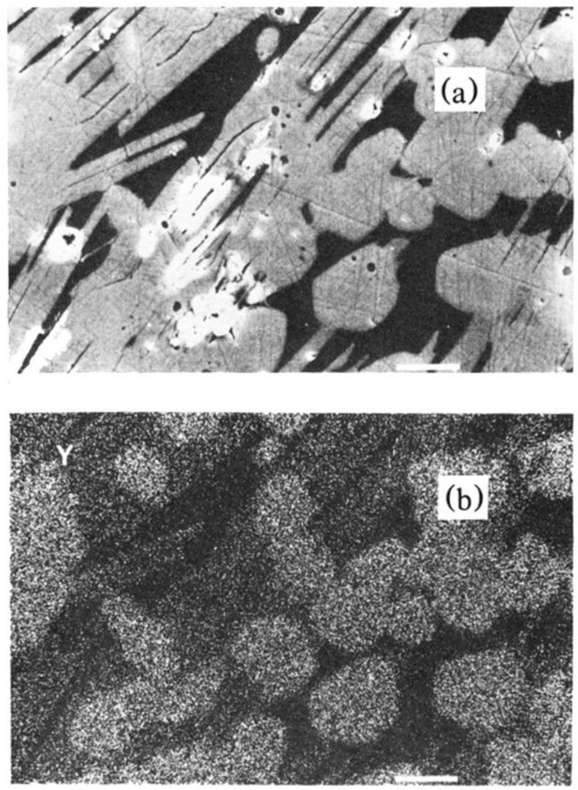

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