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M. T. Causa, S. M. Dutrús, C. Fainstein, H. R. Salva, L. B. Steren, M. Tovar, and R. Zysler

Centro Atómico Bariloche and Instituto Balseiro, Comisión Nacional de Energía Atómica and Universidad Nacional de Cuyo, 8400 Bariloche, Rio Negro, Argentina

We report normal and superconducting properties of Fe-doped $YBa_2Cu_3O_{7-\delta}$. Results from x-ray powder diffraction, electrical resistivity, magnetic susceptibility, and ESR measurements are presented. The structural effects of doping are described and their correlation with the change in superconducting properties is discussed. Similarities with the superconducting properties of oxygen deficient $YBa_2Cu_3O_{7-\delta}$ are analyzed. The comparison of the average distance between impurities (or oxygen vacancies) with the coherence length of the material suggests the existence of a nonhomogeneous order parameter in the region of low concentration of defects.

The recent finding of new superconductors[1,2] with high transition temperatures has raised the question of whether the microscopic mechanism leading to superconductivity is the same as in known superconductors. Part of the problem is to determine what is the response of these materials to the presence of magnetic impurities. In the family of compounds $ABa_2Cu_3O_{7-\delta}$ the A atoms may be yttrium or almost any element of the rare-earth group. It has been found so far[3,4] that the superconducting transition temperature, $T_c \simeq 90$ K, is not affected even when the A atoms carry a well-defined magnetic moment such as in the case of Gd, Dy, or Er. This fact is usually explained through the argument that the A atoms occupy sites in the crystal structure isolated from the Cu-O planes where superconductivity is believed to occur. If this is the case, it is an interesting problem to study the effect of magnetic moments associated with atoms located within these superconducting planes. We report results on Fe-doped samples of $YBa_2Cu_3O_{7-\delta}$, assuming that Fe atoms most probably replace Cu ions in the lattice. Preliminary data[5] showed that Fe addition considerably affects the crystal structure of the material. We present a detailed account of the x-ray patterns, electrical resistivity, magnetic susceptibility, and electron spin resonance (ESR) measurements as a function of the Fe concentration.

The samples were prepared from $BaCO_3$, Y_2O_3, and a mixture of Cu and Fe oxides coprecipitated from an aqueous solution of the corresponding nitrates. The starting materials were thoroughly mixed in appropriate amounts for the nominal concentration $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$, pressed into cylindrical shape, and allowed to react in an O_2 atmosphere at 950 °C for 12 h. The samples were then slowly cooled to room temperature, always in an O_2 atmosphere.

X-ray powder diffractograms were made at room temperature and two regions were identified as a function of the Fe concentration. A first region, named I in Fig. 1, was observed for $0 \leqslant x \leqslant 0.01$ and corresponds to the orthorhombic structure stable at room temperature[6] for the undoped compound. In this region the orthorhombic distortion is slightly reduced with the addition of Fe. A small but monotonous increase of the atomic cell volume with the Fe content was also determined beyond the experimental uncertainty, giving an indication of the incorporation of the Fe atoms into the structure. For Fe concentrations above $x \simeq 0.03$ a tetragonal phase was always observed (region II) with lattice parameters close to those obtained for the tetragonal phase[7] of pure $YBa_2Cu_3O_{7-\delta}$ above 750 °C. Samples with $0.01 < x < 0.03$ formed in either structure without a definite relationship to the nominal Fe concentration. Our samples always showed in their x-ray diffractograms the presence of other phases, which we have identified to be mainly the cubic phase $BaCuO_2$ and the orthorhombic "green phase" Y_2BaCuO_5. Another phase not yet identified was also present in the intermediate region around $x = 0.02$ characterized by a relatively strong peak corresponding to a lattice spacing $d = 2.865(5)$ Å. This peak was also observed in samples with $x > 0.10$. The observed x-ray patterns were compared to a standard sample prepared with a controlled mixture of three major phases present in the samples. As a result we estimate the impurity phases content to be in the range from 0.5 to 6 wt. %.

The electrical resistivity of low Fe concentration samples ($x \leqslant 0.003$) showed a metalliclike temperature dependence from room temperature down to 100 K and a sharp superconducting transition, as indicated in Fig. 2. Samples with $x \geqslant 0.005$ displayed a semiconductorlike resistivity and a considerable broadening of the superconducting transition. In the case of samples with tetragonal structure the superconducting transition was also shifted to lower temperatures.

Magnetic susceptibility measurements were made using a Faraday balance magnetometer, in the normal state of both "pure" and Fe-doped samples in order to determine their magnetic characteristics. Undoped $YBa_2Cu_3O_{7-\delta}$ samples showed a weak paramagnetic behavior. The temperature-independent component of the susceptibility, measured for two different samples, indicates a Pauli paramagnetic susceptibility $\chi_p = 3.5 \times 10^{-4}$ and 4.8×10^{-4} emu/mole Y, after including corrections for the core diamagnetism but not for the Landau diamagnetism of the conducting electrons. The corresponding values of the parameter γ in a free-electron model are 25 and 34 mJ/mole Y K^2 for the two samples. Although a comparison with other reported mea-

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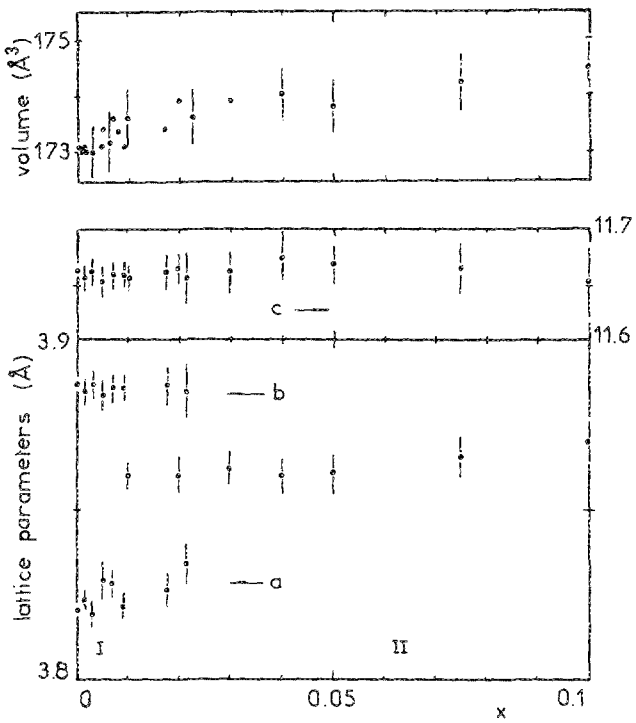

FIG. 1. Lattice parameters and unit-cell volume vs Fe concentration.

surements shows that there is considerable scattering of the values of χ_p depending probably on the particular sintering conditions of the material, the values are in reasonable agreement with those derived from the specific-heat anomaly[8,9] at the superconducting transition, assuming a Bardeen–Cooper–Shrieffer (BCS) relation $\Delta C/\gamma T = 1.43$.

A small temperature-dependent component was also observed in the undoped samples. It followed a Curie–Weiss paramagnetic law, and the Curie constants for the two samples measured are consistent with average magnetic moments of $0.26\mu_B$ and $0.44\mu_B$ per Cu ion, respectively. In order to estimate how much of the measured moments is actually associated with the $YBa_2Cu_3O_{7-\delta}$ phase we measured separately the magnetic susceptibility of the other phases known to be present in our samples. We found that both Y_2BaCuO_5 and $BaCuO_2$ are paramagnetic above 55 K (the lowest temperature reached in the measurements) with effective moments of $1.74\mu_B$ and $1.93\mu_B$ per Cu ion, respectively. Y_2BaCuO_5 had an antiferromagnetic Curie–Weiss temperature $\theta = 43$ K and $BaCuO_2$ a ferromagnetic $\theta = 24$ K. From these values and the estimated concentration of these two phases in our samples we conclude, in agreement with other authors,[10,11] that most of the measured magnetic moment is originated in the impurity phases. This fact is important because the Fe-doped samples also showed a Curie–Weiss paramagnetic behavior and the measured Curie constants had to be corrected for the estimated contributions from the impurity phases. An average effective moment $\mu_{\text{eff}} = 5.2(5)\ \mu_B$ per Fe ion was then determined for the samples in region II. For low Fe concentration samples the contribution of impurity phases was comparatively larger and did not allow a precise determination of the magnetic moment.

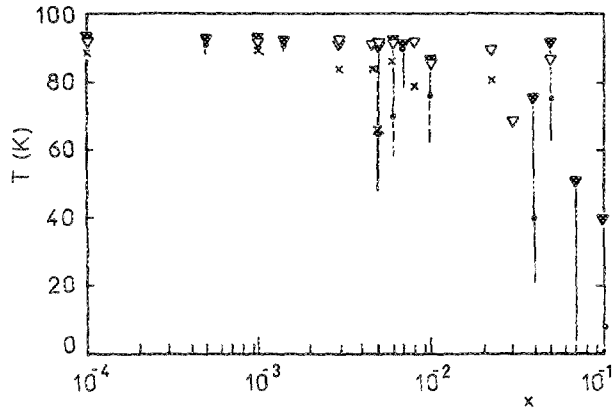

FIG. 2. Characteristic temperatures of the superconducting transition vs Fe concentrations: (▼) onset of the resistive transition, (▽) onset of the magnetic transition, (◉) midpoint resistive, (×) 6% Meissner effect.

ESR experiments at room temperature showed in all cases an absorption line at an average g value of 2.09. The g value and line shape observed allowed us to identify this spectrum as arising primarily from the Y_2BaCuO_5 phase (pure $BaCuO_2$ shows no ESR signal for the same sensitivity). The observed ESR intensities correlate with the amount of this impurity phase determined from the x-ray analysis. No other ESR line that could be associated with Fe ions was observed.

The superconducting transitions, as measured by the magnetic susceptibility when cooling in a magnetic field of 50 G, followed the same trend of the resistive transitions. For the samples in region I the onset temperature departed very little from the values of the undoped material, the transitions broadened with the increase in the Fe content, and the diamagnetic susceptibility measured at low temperatures became smaller. Figure 2 shows the measured onset temperatures and also the temperatures where the diamagnetic signal reaches a value of 8×10^{-4} emu/g. This point corresponds to a 6% Meissner effect (for a density of 6 g/cm^3), and it has been taken as an indication of the width of the transition. Tetragonal samples showed also a larger depression of the superconducting transition temperature.

As a conclusion, we can say that Fe doping of $YBa_2Cu_3O_{7-\delta}$ produces changes in the superconducting properties that clearly correlate with structural modifications of the crystal lattice. Low concentrations of Fe ($x \lesssim 0.01$) reduce the orthorhombic distortion of the lattice and large concentrations ($x \gtrsim 0.03$) stabilize a tetragonal structure. Associated with these changes the temperature dependence of the electrical resistivity becomes semiconductorlike and the superconducting transitions broaden and shift to lower temperatures. These effects are not unique of the Fe doping of the samples. The same behavior has been observed[12] for doping with nonmagnetic elements such as Zn, or when the samples are annealed in reducing atmospheres.[13] Similar effects have also been observed when relatively large rare-earth ions occupy the A sites. In this case the lattice parameters correlate with the ionic radii of the rare-earth ion, and there is also a systematic trend of de-

creasing orthorhombic distortions with increasing ionic radii.[5] Associated with this behavior the superconducting transitions of the compounds with light rare earths tend to display broad superconducting transitions.[4]

It is interesting to observe the correlation of the impurity concentration regions where structural and superconducting changes occur, with the average distance between impurities, d. Assuming that Fe atoms randomly replace Cu ions in the lattice, we see that the characteristic concentration range where the tetragonal structure appears ($0.01 \lesssim x \lesssim 0.03$) corresponds to a mean separation between Fe atoms from three to five lattice parameters, suggesting that this is the minimum length required for the linear Cu-O chains in order to give rise to a long-range orthorhombic distortion of the lattice. On the other hand, the Fe concentration where the superconducting transition starts to broaden ($x \simeq 0.003$), corresponds to $d \simeq 27$ Å, which is remarkably close to the coherence length $\xi(0) = 34$ Å reported for the undoped material.[14]

Comparison with data on samples with reduced oxygen content[13] shows that there is also a region around $\delta = 0$ where the superconducting transition is not affected by a partial oxygen depopulation of the Cu-O chains. This region extends up to $\delta \simeq 0.16$, corresponding to a mean distance between oxygen vacancies of $\simeq 25$ Å, again of the order of the coherence length.

This interesting behavior of the two systems in the limit of dilute defects may be related to the existence in these oxide superconductors of a nonhomogeneous order parameter as has been suggested[15] to explain magnetic flux penetration experiments. The possibility of observing this kind of behavior is favored in these materials because it is possible to find experimentally a region where the mean distance between defects affecting superconductivity is larger than the coherence length.

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