Competition between Superconductivity and Antiferromagnetism in Cu(2) Layers of $Y_{1-x}Pr_xBa_2Cu_{3-y}M_yO_z$, $M = $ Fe, Co, Zn

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The antiferromagnetic (AFM) and superconducting (SC) phase transition temperatures of $Y_{1-x}Pr_xBa_2Cu_{3-y}M_yO_z$, $M =$ Fe,Co,Zn, were studied by magnetometry and ^{57}Fe Mossbauer spectroscopy. For $z \sim 7$, substitutions at all sites except those in the CuO_2 planes (Pr,Fe,Co) cause SC to disappear at $x_c = 0.5$ or $y_c = 0.4$ and AFM to appear above x_c and y_c. For $z \sim 6$, AFM persists for all x and y values. On the other hand, substitution in the Cu(2) planes (Zn) suppresses both SC at $y_c = 0.24$ for $z \sim 7$ and AFM for $z \sim 6$. No AFM is seen for $z \sim 7$.

A central issue regarding high-T_c superconductivity is whether or not magnetic interactions are important in stabilizing the superconducting electronic ground state as proposed in many theories.[1] Evidence for magnetic ordering of Cu(2) layers in $YBa_2Cu_3O_z$ (YBCO) was provided by muon-spin-relaxation (μSR),[2] neutron-scattering experiments,[3] and Mössbauer spectroscopy,[4] and the oxygen-content phase diagram is now well established. This phase diagram[5] shows that for $z > 6.45$ the system is orthorhombic, metallic, and superconducting with T_c decreasing as z decreases. For $z < 6.45$ the system becomes tetragonal, semiconducting, and antiferromagnetic with a Néel temperature of $T_N = 420$ K for $z \sim 6$. The magnetic structure is composed of strong nearest-neighbor antiferromagnetic coupling of the spins within the CuO_2 planes, with antiferromagnetic alignment of the nearest-neighbor spins in the adjacent planes. The magnetic moments are constrained to lie in the planes. The phase diagram of $(La,M)_2CuO_4$, which resembles that of YBCO, also exhibits dramatic behavior such as structural changes, 3D antiferromagnetism, disordered magnetism, and superconductivity as a function of hole doping.[6] In the third class of high-T_c superconductors such as Bi-Sr-Cu-Cu-Ca-O, substition of Y for Ca changes the electronic and magnetic properties and a quite similar phase diagram involving superconductivity and magnetism is obtained.[7] There is no conclusive evidence for coexistence of both phenomena in the same composition.[8] From an experimental viewpoint, it is thus of great interest to study and understand the delicate interplay between these two phenomena.

The question we tried to answer is whether the superconductive-magnetic phase diagram for YBCO is unique and depends only on oxygen concentration, or whether substitution of other elements into the system would lead to similar phase diagrams. The present Letter deals with this interrelation between superconductivity and magnetism in the wide family of compounds $Y_{1-x}Pr_xBa_2Cu_{3-y}M_yO_z$, where M stands for Fe, Co, and Zn.

The YBCO phase contains both CuO_2 planes [denoted Cu(2)] and CuO chains [denoted Cu(1)]. We show here that in oxygen-rich samples, when Y is substituted by Pr and Cu(1) is substituted by Fe or Co, with x or y close to the value of the disappearance of superconductivity, a static antiferromagnetic ordering is induced in the Cu(2) site, in a way which is very similar to that observed in $YBa_2Cu_3O_z$ with the removal of oxygen.[5] For oxygen-deficient samples $(z \sim 6)$ all the compounds are antiferromagnetically ordered and T_N changes very little with x or y. On the other hand, in oxygen-rich samples, substitution of Cu(2) by Zn in the CuO_2 planes suppresses superconductivity, but magnetic order is never found. For the $z \sim 6$ materials, T_N depends on Zn concentration and antiferromagnetism disappears approximately at the same concentration where superconductivity disappears for the oxygen-rich samples.

The ceramic system $Y_{1-x}Pr_xBa_2Cu_3O_7$ and $YBa_2Cu_{3-y}M_yO_{7-\delta}$ were prepared by conventional methods.[9] X-ray-diffraction studies were performed to ensure the purity of the compounds. The oxygen-deficient samples were obtained by quenching the materials from 900 °C to liquid nitrogen. Using the published data on the temperature and oxygen dependence of the oxygen concentration in the YBCO system[10] we estimate the oxygen concentration in the quenched sample as 6.1–6.2. dc susceptibility measurements in low fields were carried out in a PAR vibrating magnetometer to determine T_c of the samples. In order to determine the magnetic nature of the Cu sublattices, all samples were doped with at least 1% ^{57}Fe for Mössbauer studies. Mössbauer spectroscopy studies were performed using a conventional constant-acceleration spectrometer and a 100-mCi Rh-Co^{57} source. The spectra at various temperatures were least-squares fitted with several subspectra corresponding to the various inequivalent iron sites. Mössbauer studies[4] and differential anomalous x-ray scattering[11] clearly indicate that the Fe atoms occupy predominantly the Cu(1) site, with an increasing fraction of Fe residing in the Cu(2) sites as the total amount of dopant increased. When the Cu(2) sublattice becomes magnetically ordered, it produces an exchange field at the iron located in the Cu(2) sites. The iron nuclei experience a magnetic hyperfine field leading to a six-line pattern in the ob-

served Mössbauer spectra.[4] In a recent paper we have shown that in $YBa_2Cu_3O_{6+\delta}$, T_N is not affected by the presence of Fe, and that Fe is thus a reliable probe of the magnetic behavior of the Çu(2) sites.[4]

Phase diagram of $YBa_2Cu_{3-y}Fe_yO_{7+\delta}$. — Substitution for Cu by Fe results in an orthorhombic-tetragonal structure transition at $y = 0.06-0.09$, and produces drastic changes in T_c. The solubility limit of Fe in YBCO is $y = 0.8$. Since Fe ions have a larger valence than Cu, they attract oxygen to maintain charge neutrality. Therefore we assign $z = 7 + \delta$ and $z = 6 + \delta$ for oxygen-rich and quenched samples, respectively. The value of δ is proportional to y (one oxygen atom for two Fe atoms[12]) and is not necessarily the same for $z = 7$ and $z = 6$ systems. Measurements by us[9] and others[13] established that T_c remains constant and equal to 90 K up to the orthorhombic-tetragonal transition and then decreases continuously to less than 4.2 K at $y > 0.40$. Several groups have measured the variation of T_c with y and the change of T_c with y obtained by different groups differs somewhat from group to group. The mean values for the concentration dependence of T_c with y for Fe are shown in Fig. 1. Upon increasing y further, the compounds become semiconductors and our Mössbauer measurements show that simultaneously antiferromagnetism associated with the Cu(2) ions develops. Some Mössbauer spectra of $YBa_2Cu_{2.25}Fe_{0.75}O_{7+\delta}$ are shown in Fig. 2. The central part of the Mössbauer spectra in Fig. 2

corresponds to Fe which replaces copper in the Cu(1) site.[4] The well-defined magnetic sextet is attributed to iron which replaces copper in the Cu(2) sites and orders antiferromagnetically. The magnetic hyperfine field at 90 K is 495 kOe. As the temperature is raised, the magnetic splitting decreases and the Néel temperature can be obtained. In Fig. 1 the change of T_N as a function of y is displayed. T_N decreases gradually from 390 K for $Y = 0.75$ to 330 K for $y = 0.50$ and then drops sharply to 29 K for $y = 0.45$. No magnetic structures are observed in the superconducting range where $y < 0.40$. This superconducting-magnetic phase diagram is very similar to that obtained for oxygen-content dependence (z) in $YBa_2Cu_3O_z$.[5] A phase diagram similar to that shown for Fe in Fig. 1 is obtained for Co replacing Cu.

Figure 1 shows that for the quenched oxygen-poor $YBa_2Cu_{3-y}Fe_yO_{6+\delta}$ samples, T_N of the Cu(2) sites depends weakly on y and increases from 410 K for $y = 0$ to 430 K for $y = 0.75$. In contrast to the Mössbauer spectra shown in Fig. 2, in the quenched samples we observe a broadening of the central part of the spectra in addition to the sextet corresponding to iron in the Cu(2) sites.[14] This broadening is attributed to a second independent magnetic ordering of Fe in the Cu(1) site with $T_N = 210$ K (Fig. 1). Our results differ slightly from those obtained in Ref. 15. Since most of the magnetic Fe ions reside in the Cu(1) site,[4,11] they encourage magnetic ordering on the chain site and dictate its nature. The situ-
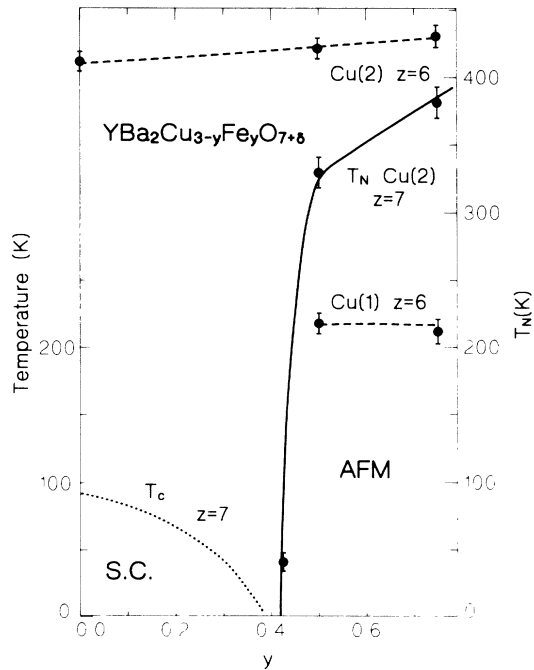

FIG. 1. Phase diagram for oxygen-rich $YBa_2Cu_{3-y}Fe_yO_{7+\delta}$ as a function of Fe concentration. T_c for the superconducting (SC) phases and T_N for the antiferromagnetic (AFM) phases are shown. The dashed lines show T_N values for the quenched samples in both Cu(1) and Cu(2) sites.
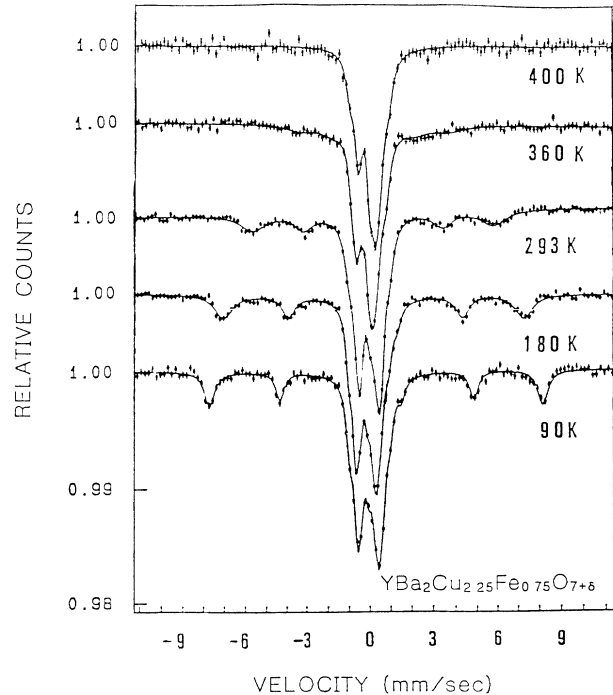

FIG. 2. Mössbauer spectra of $YBa_2Cu_{2.25}Fe_{0.75}O_{7+\delta}$ at several temperatures. The magnetic splitting, which is attributed to Fe in the Cu(2) sites, decreases with increasing temperature and disappears at T_N.

ation is different in the Cu(2) sites where the concentration of Fe is only a small fraction of that in the Cu(1) site.

Phase diagram of $Y_{1-x}Pr_xBa_2Cu_3O_z$.— It is well known that in the orthorhombic $Y_{1-x}R_xBa_2Cu_3O_7$ system (R denotes rare earth) T_c does not depend on x when R is a trivalent rare-earth element.[16] An exception to this behavior is $PrBa_2Cu_3O_7$ which is orthorhombic, yet not superconducting. The valency of Pr is still controversial.[17] Neutron-diffraction measurements show that its oxygen concentration is 7.[18] In the orthorhombic $Y_{1-x}Pr_xBa_2Cu_3O_7$ system it is assumed therefore that the oxygen concentration remains 7 for the entire system, T_c decreases sharply with increasing x (Refs. 18–21), and the variation of T_c (and T_N for the Pr sublattice) in $Y_{1-x}Pr_xBa_2Cu_3O_7$ was reported by ourselves[19] and others.[18,20] Clearly, T_c decreases with increasing x, and for $x > 0.5$ the compounds are not superconducting. Moreover, using the Mössbauer technique on iron-doped samples, we showed that for $x > 0.5$ the Cu(2) sites are magnetically ordered.[19] T_N obtained for $x = 0.6$ is 230 K and it increases gradually to 300 K for $x = 0.8$ and to 325 K for $x = 1$. A similar behavior was also obtained in zero-field muon-spin-relaxation measurements.[21] The disappearance of superconductivity and the appearance of antiferromagnetism in both Cu(2) and Pr sites is probably associated with strong Pr $4f$ electron hybridization.[19,20] It was also shown[19] that T_N values for the quenched samples ($z \sim 6$) depend weakly on x

FIG. 3. Superconducting-magnetic phase diagram for $YBa_2Cu_{3-y}Zn_yO_z$. Note the absence of magnetic ordering at $y = 0.3$ in both fully oxygenated (square) and quenched (circle) samples.

and range from 350 K for $x = 1$ to 420 K for $x = 0$.

We have shown above the similarity between the phase diagrams of $YBa_2Cu_3O_z$,[5] $YBa_2Cu_{3-y}M_yO_{7+\delta}$ (M =Fe,Co) (Fig. 1), and $Y_{1-x}Pr_xBa_2Cu_3O_7$,[19] in which the competition between superconductivity and magnetism leads to the appearance of antiferromagnetism in the vicinity of the disappearance of superconductivity.

Phase diagram of $YBa_2Cu_{3-y}Zn_yO_z$.— A unique exception to the common behavior discussed above is observed in the $YBa_2Cu_{3-y}Zn_yO_7$ system. X-ray[11] and neutron-diffraction[22] measurements indicate that in the Zn-doped system, the crystal structure remains orthorhombic up to $y = 0.3$. Several measurements have shown that divalent Zn ions preferentially substitute Cu in the Cu(2) sites,[22] or distribute roughly equally among Cu(2) and Cu(1) sites.[11] [An equal distribution means that about 70% of Zn enters Cu(2) sites, since the number of Cu(2) atoms in the unit cell is twice that of Cu(1) atoms.] The oxygen concentration up to $y = 0.3$ remains almost unchanged on introduction of divalent Zn.[12,23] The general result is that substituting small amounts of Zn for Cu strongly inhibits superconductivity and for $y = 0.24$, T_c vanishes (Fig. 3). This implies that T_c is more affected when the doping occurs in the CuO_2 planes than in the CuO chains. Our Mössbauer measurements on 1%-^{57}Fe-doped samples definitely show that also in this system, most of the Fe ions occupy the Cu(1) site and only about 20% of Fe resides in the Cu(2) sites. The Mössbauer measurements show that the fully oxygenated samples, which are not superconducting ($y > 0.24$), also do *not* display magnetic order in the CuO_2 planes. Moreover, unlike in the systems mentioned above (Fig. 2), the magnetic ordering temperatures T_N of the quenched samples in this system depend on Zn concentration (Figs. 4 and 3), and antiferromagnetism disappears approximately at the same concentration ($y = 0.30$) where superconductivity disappears for the oxygen-rich samples, $y = 0.24$. Figure 4(a) displays some Mössbauer spectra of ^{57}Fe in $YBa_2Cu_{2.88}Zn_{0.12}O_{6+\delta}$ at several temperatures. As described above, the central part of the Mössbauer spectra corresponds mainly to Fe which occupies the Cu(1) site. The well-defined magnetic sextet, which is attributed to iron residing in the Cu(2) sites, disappears at $T_N = 230$ K, much lower than $T_N = 420$ K found in $YBa_2Cu_3O_{6+\delta}$. The magnetic hyperfine field observed at 90 K is 370 kOe. In all samples we identify above T_N, the typical paramagnetic quadrupole doublet is due to iron in the Cu(2) site.[4,14] [Isomer shift $= 0.25(1)$ mm/s and $eqQ/2 = 0.67(1)$ mm/s.] This doublet is also observed in samples with $y = 0.30$ in both fully oxygenated and quenched samples at all temperatures, thus proving that Fe also enters into the Cu(2) site. For all Zn concentrations measured its relative intensity accounts for about 20% of the overall spectral area and Fig. 4(b) exhibits (on an expanded scale) this doublet obtained in quenched $YBa_2Cu_{2.7}Zn_{0.3}O_{6+\delta}$ (doublet A). The ab-
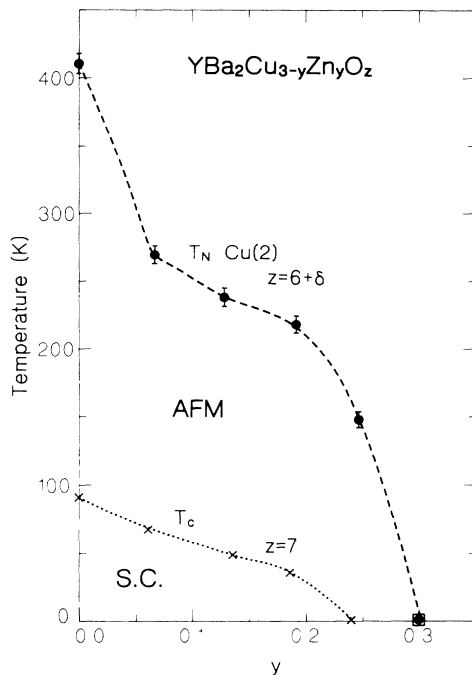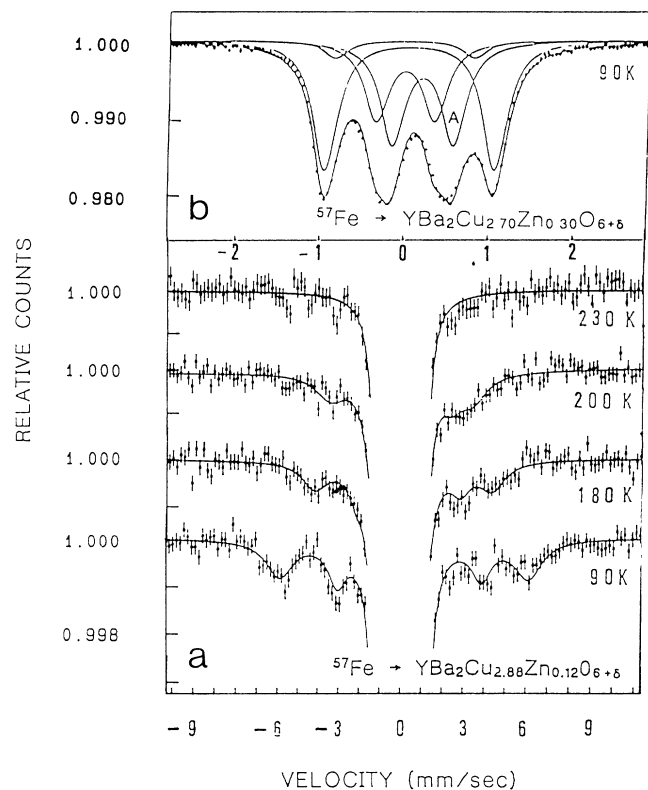
FIG. 4. (a) Mössbauer spectra of 1%-^{57}Fe-doped YBa$_2$-Cu$_{2.88}$Zn$_{0.12}$O$_{6+\delta}$ at several temperatures. The magnetic splitting disappears at $T_N = 230$ K. (b) Mössbauer spectrum of ^{57}Fe-doped YBa$_2$Cu$_{2.7}$Zn$_{0.3}$O$_{6+\delta}$ in which the doublet corresponding to Fe in the Cu(2) sites (doublet A) is observed. Note the expanded velocity scale for this spectrum.

sence of magnetic order in Zn-rich samples, independent of the amount of oxygen, demonstrates that divalent Zn in the Cu(2) sites inhibits long-range magnetic correlations as well as reducing superconductivity.

In summary, the superconducting-magnetic phase diagrams with various cationic substitutions in oxygen-rich YBCO with different oxygen concentrations show that whenever the doping is *not* in the CuO$_2$ planes a similar behavior is observed: In the vicinity of the disappearance of superconductivity, the Cu(2) moments order antiferromagnetically. Substitution of Zn *in* the CuO$_2$ planes destroys both superconductivity and magnetism at approximately the same Zn concentration.

The experimental observations reported in this paper indicate that in oxygen-rich samples, superconductivity and magnetism are confined to the CuO$_2$ planes. Substitutions affecting the number of mobile charge carriers (holes) in these planes, either by substituting Cu(1) by Fe or Co, oxygen by vacancies, or Y by Pr, all suppress superconductivity and enhance magnetic order. On the other hand, destruction of the periodicity and regularity in the Cu^{2+}O$_2$ planes, even by diamagnetic Zn^{2+} is

sufficient to suppress both superconductivity and magnetism. This observation indicates the delicate interplay between the two phenomena and might serve as a guideline for theories that attempt to describe the importance of magnetic interaction in the high-T_c superconductors.

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