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Superconductivity and magnetic order in the Cu(2) planes in Fe-doped $YBa_2Cu_4O_8$

I. Felner, I. Nowik, B. Brosh, D. Hechel, and E. R. Bauminger
Racah Institute of Physics, The Hebrew University, Jerusalem 91904, Israel

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Mössbauer spectroscopy, magnetic susceptibility, and powder x-ray-diffraction measurements were used to study superconductivity and magnetic order in $YBa_2(Cu_{1-x}Fe_x)_4O_{8+\delta}$. T_c is reduced with increasing Fe concentration and superconductivity is totally depressed for $x \geq 0.04$. The Mössbauer spectra show that at concentrations where superconductivity disappears magnetic order, probably antiferromagnetism, is formed in the Cu(2) site. The phase diagram obtained is similar to those previously obtained for $Y_{1-x}Pr_xBa_2(Cu_{1-y}Fe_y)_3O_{7+\delta}$ [I. Felner *et al.*, Phys. Rev. Lett. **65**, 1945 (1990)]. In the superconducting region Fe atoms occupy only the Cu(1) sites and the ^{57}Fe Mössbauer spectrum contains only one doublet.

Bulk samples of the high-T_c superconductor $YBa_2Cu_4O_8$ (hereafter referred to as 1:2:4) have recently been synthesized by various groups and by different methods. Morris *et al.*[1] synthesized bulk 1:2:4 samples by a high-oxygen-pressure technique. These samples exhibited a superconducting transition at around 80 K. Cava *et al.*[2] were successful in synthesizing the 1:2:4 phase in a powder form under 1-atm oxygen pressure by utilizing a catalyst such as alkali-metal carbonates. X-ray[3,4]- and neutron[5]-diffraction studies revealed that the 1:2:4 structure is closely related to $YBa_2Cu_3O_7$ (designated 1:2:3 below), but with an additional Cu-O chain in the unit cell. Each unit cell contains two Cu-O chains [denoted Cu(1)] and two CuO_2 planes [denoted Cu(2)]. This leads to a much longer *c* lattice parameter of 27.20 Å and a smaller orthorhombicity (0.8% in the 1:2:4 phase, 1.18% in the 1:2:3 phase). Furthermore, the 1:2:4 compound has excellent thermal stability of oxygen content up to 800 °C since oxygen is neither lost nor gained during heating and cooling[1,2] and the well-known tetragonal-orthorhombic phase transition of the 1:2:3 structure at high temperature is absent. When a 1:2:4 sample was heated at 815 °C for several hours and then quenched to liquid-nitrogen temperature, the superconducting properties of the material were retained.[6]

It is by now well established that in the 1:2:3 systems there is competition between superconductivity and antiferromagnetism in the Cu(2) planes.[7–10] In the orthorhombic $YBa_2Cu_3O_z$ system, T_c is dramatically affected by oxygen content and for $z < 6.4$ the samples are tetragonal, semiconducting, and the Cu(2) sites are antiferromagnetically ordered. T_N increases sharply with decreasing z, from $T_N = 0$ K for $z = 6.5$ to $T_N = 415$ K for $z = 6.0$.[7] The magnetic structure is composed of strong nearest-neighbor antiferromagnetic coupling of the spins within the Cu(2) planes, with antiferromagnetic alignment of the nearest-neighbor spins in the adjacent planes. Using the Mössbauer technique on iron-doped samples it was shown[8] that T_N (for $z = 6.0$) is not affected by the presence of Fe. T_N determined by Mössbauer technique agrees perfectly with T_N measured by neutron diffraction and muon-spin-relaxation measurements, which proves that Fe is thus a reliable probe of the magnetic behavior of the Cu(2) sites. It was shown that this interrelation between superconductivity and magnetism is found in a wide family of catonic substitutions in the oxygen-rich 1:2:3 system.[9,10] We have shown that whenever various cations are doped in sites outside the Cu(2) planes, in the vicinity of the disappearance of superconductivity, the Cu(2) moments order antiferromagnetically.[10]

Here detailed studies of $YBa_2(Cu_{1-x}Fe_x)_4O_8$ with x ranging from $x = 0$ to $x = 0.1$ are presented. Several experimental techniques were used and a detailed phase diagram which exhibits a region of superconductivity and a region of magnetic order of the Cu(2) sites was obtained. It is shown that partial substitution of Cu by Fe sharply reduces the T_c of the system and for Fe concentration exceeding 4 at.% the materials are not superconducting. Moreover, in these later samples a static magnetic ordering of Cu(2) sites is found. Thus the 1:2:4 system behaves similarly to the 1:2:3 system discussed above. The observed magnetic order in the Cu(2) site of the 1:2:4 system is probably antiferromagnetic, in analogy with the 1:2:3 system. The ^{57}Fe Mössbauer spectra of the 1:2:4 system show that at low Fe content the iron atoms occupy only the Cu(1) sites, with an increasing fraction occupying the Cu(2) sites as the total amount of dopant increases.

$YBa_2(Cu_{1-x}Fe_x)_4O_8$ samples were prepared by a solid-state reaction of stoichiometric mixtures of the constituent oxides, following the procedure described recently by Pooke *et al.*[11] The stoichiometric mixtures, with an addition of 0.2-mol $NaNO_3$, were prereacted as a loose powder for 30 min at above 600 °C. The powders were then pressed into pellets, and reacted at 815 °C for 12 h in flowing oxygen, and then reground. This procedure was applied at least four times. The best materials are obtained when the samples are quenched from 815 °C to ambient temperature, then heated again to 800 °C and furnace cooled under flowing oxygen to room temperature. X-ray-diffraction studies were performed to determine the crystallographic structure and to insure the purity of the compounds. The Mössbauer spectroscopy studies were performed using a conventional constant-acceleration spectrometer and a 100 mCi ^{57}Co:*Rh* source. The spectra at various temperatures were least-squares fitted with two subspectra corresponding to the two inequivalent iron sites. Magnetic dc susceptibility measurements in low fields as a function of temperature, carried out in a PAR vibrating-sample magnetometer, determined the T_c of the samples.

(a) *Crystal structure measurements.* Because of the structural complexity of the 1:2:4 phase and the many parameters involved in the fitting process, it is important to be sure that the basic undoped material is providing reliable results. X-ray powder measurements on $YBa_2(Cu_{1-x}Fe_x)_4O_{8+\delta}$ samples indicate that all the samples are single phases. Least-squares refinement of the crystallographic unit-cell parameters yield $a = 3.833$ Å, $b = 3.873$ Å, and $c = 27.19$ Å for pure orthorhombic 1:2:4, in complete agreement with Ref. 11. Figure 1 shows the lattice parameters for the undoped and various Fe-doped samples determined at room temperature. From our refinement, the sample with $x = 0.025$ is found to be orthorhombic, and samples with $x \geq 0.05$ are found to be tetragonal within fitting errors. The c lattice parameter decreases slightly with x in the orthorhombic phase and remains practically constant in the tetragonal structure. The tetragonal phase induced by the doping of Fe in 1:2:4 is very similar to that obtained in the 1:2:3 Fe-doped system.[12] More details concerning the crystal structure analysis will be published elsewhere.

(b) dc *magnetization measurements.* The variation of T_c in $YBa_2(Cu_{1-x}Fe_x)_4O_{8+\delta}$ with x was studied in a dc field of about 20 Oe in the field-cooled process. The data obtained are exhibited in Fig. 2. Clearly, T_c decreases linearly with x at a rate of about 23-K/at.% Fe [i.e., $T_N = 82(1)$ K, 59(1) K, and 26(1) K, for $x = 0.00$, 0.01, and 0.025, respectively] and for $x = 0.04$ the compound is not superconducting any more. The present data agree perfectly with the values of T_c for $0 < x < 0.02$ published in Ref. 13. Upon increasing x further, the compounds are not superconducting and our Mössbauer measurements show the simultaneous development of magnetic order associated with the Cu(2) ions. The observed magnetic order is probably antiferromagnetic, as in the 1:2:3 system. Neutron-diffraction studies are needed to confirm the magnetic structure.

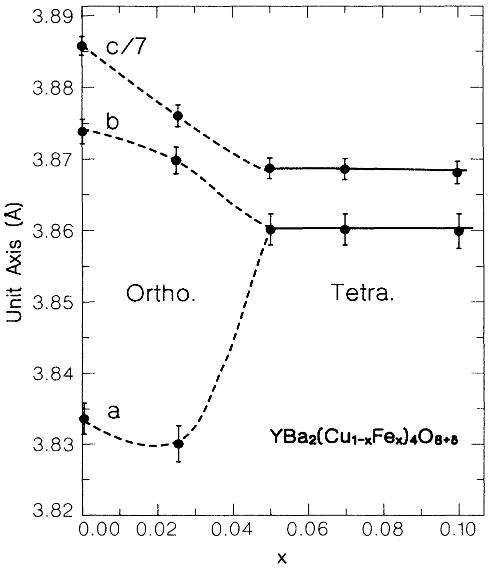

FIG. 1. Concentration dependence of unit-cell parameters of $YBa_2(Cu_{1-x}Fe_x)_4O_{8+\delta}$ at room temperature. Doping of Fe induces an orthorhombic-tetragonal phase transition at about $x = 0.05$.

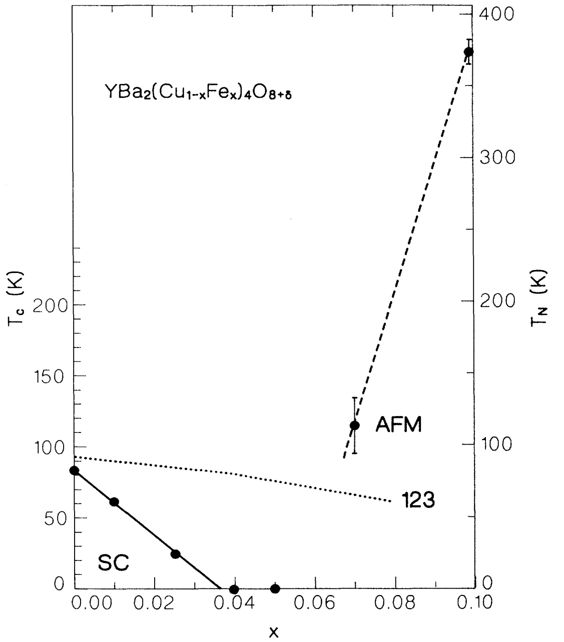

FIG. 2. Phase diagram for $YBa_2(Cu_{1-x}Fe_x)_4O_{8+\delta}$ as a function of Fe concentration. Extrapolated values for T_c of the superconducting phase and T_N of the antiferromagnetic phase are shown as solid and dashed lines, respectively. For comparison, the dotted line shows the variation of T_c as a function of Fe concentration in the $YBa_2Cu_3O_7$ (1:2:3) system.

It should be noted that in the $YBa_2(Cu_{1-y}Fe_y)_3O_{7+\delta}$ system, the variation of T_c with y was studied by several groups and the change of T_c with y obtained by different groups differ from one group to another. These differences simply arise from the synthesis history of the materials. However, the mean values for the concentration dependence of T_c on y (Refs. 9 and 10) shows definitely that for $y > 0.13$, T_c is less than 4.2 K, whereas for the 1:2:4 system T_c disappears already at $x > 0.04$ (Fig. 2). The general conclusion is that T_c in the 1:2:4 system is much more affected by Fe doping than T_c in the 1:2:3 system.

(c) *Mössbauer studies of low iron concentration in 1:2:4.* Figure 3(a) shows the Mössbauer spectrum obtained at 90 K for 2.5%-^{57}Fe-doped 1:2:4. T_c for this compound is 26 K (Fig. 2). The main information obtained from visual and computer analysis of this spectrum is that only one quadrupole doublet is present with $eqQ/2 = 0.85(1)$ mm/s and isomer shift of 0.41(1) mm/s relative to Fe metal. These parameters can be assigned to Fe^{3+} in a high spin state. We attribute this doublet to iron ions which replace copper in the Cu(1) sites. In contrast to 1:2:3, here all the iron ions in this site are

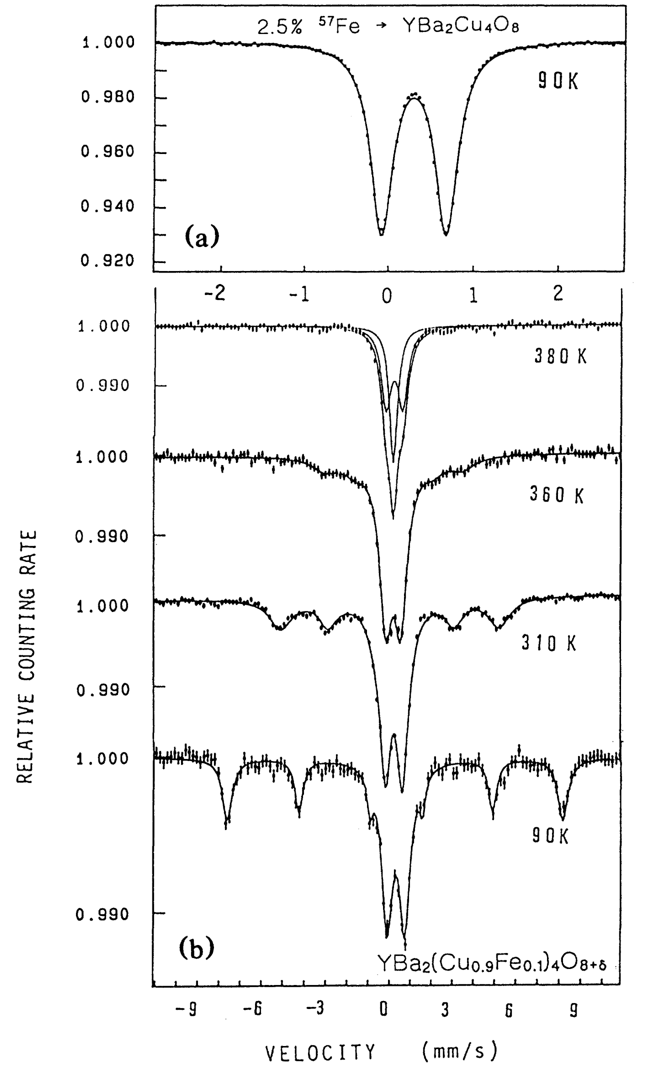

FIG. 3. (a) Mössbauer spectrum of 2.5% ^{57}Fe doped in $YBa_2Cu_4O_8$ at 90 K, which is attributed to Fe in the Cu(1) sites. Note the expanded velocity scale for this spectrum. (b) Mössbauer spectra of $YBa_2(Cu_{0.9}Fe_{0.1})_4O_{8+\delta}$ at several temperatures. The magnetic splitting, which is attributed to Fe in the Cu(2) sites decreases with increasing temperature and disappears at $T_N = 380$ K.

equivalent in terms of oxygen environment, and therefore only one well-defined doublet is observed. The presence of a small fraction of Fe ions (less than 3%) in the Cu(2) sites cannot be excluded. Since Fe ions have a larger valence than Cu, they attract oxygen to maintain charge neutrality. Therefore, we assign the oxygen concentration of the iron-doped 1:2:4 samples as $8+\delta$.

The thermal stability of the 1:2:4 superconductor is much better than that of 1:2:3, since oxygen is neither lost nor gained during heating or cooling.[1,2] In order to confirm this finding, we heated a piece of 2.5% ^{57}Fe-doped 1:2:4 sample at 815°C for about 2 h, then quenched it to liquid nitrogen. The superconducting properties of the quenched sample were retained,[6] and the Mössbauer spectrum of the quenched sample had exactly the same parameters as the unquenched sample.

As already mentioned, the 1:2:4 system permits two equally populated types of Cu sites, namely Cu(1) and Cu(2). Fe as a dopant can be expected to replace both sites and display Mössbauer spectra with at least two quadrupole doublets. The Mössbauer spectra of ^{57}Fe doped in oxygen-rich 1:2:3 samples are composed of (at least) four quadrupole doublets, corresponding to inequivalent iron sites, due to different oxygen-neighbor configurations in the Cu(1) sites.[8–10,12,14] None of the doublets observed in the 1:2:3 system resembles the single doublet obtained in the 1:2:4 compound reported here.

(d) *Mössbauer studies of high iron concentration doped in 1:2:4.* In $YBa_2(Cu_{0.9}Fe_{0.1})_4O_{8+\delta}$, which is not superconducting, we observe besides the above-mentioned doublet a well-defined magnetic sextet, which accounts for about 40% of the spectral area [Fig. 3(b)]. We attribute this sextet to iron atoms which replace copper in the Cu(2) site and order antiferromagnetically. All iron atoms in the Cu(2) site are equivalent in terms of oxygen environment and yield a well-defined magnetic spectrum. At 90 K the magnetic hyperfine field is 505(5) kOe and the quadrupole interaction is practically zero. The main effect to be seen in Fig. 3(b) is that as the temperature is raised, the magnetic splitting decreases and above $T_N = 380$ K the sextet disappears. The hyperfine field as a function of temperature is shown in Fig. 4. The central part of the spectra in Fig. 3(b) which corresponds to iron in the Cu(1) site, is fitted by one quadrupole doublet with the same parameters as in the $x=0.025$ spectrum [Fig. 3(a)]. It is noticeable that above T_N the spectrum is fitted with a doublet (60%) corresponding to Fe in the Cu(1) site and with a narrow single line (40%) which has an isomer shift of +0.41 mm/s. This singlet corresponds to iron in the Cu(2) site and results from the collapsed magnetic sextet. Thus the quadrupole interaction in the Cu(2) site is zero below and above T_N. The isomer shift for the two subspectra is the same within experimental errors.

We also measured the Mössbauer spectra for $x=0.07$ (not shown) which are very similar to those displayed in Fig. 3(b). At 90 K the magnetic hyperfine field, which accounts for 26% of the spectral area, is 320(10) kOe.

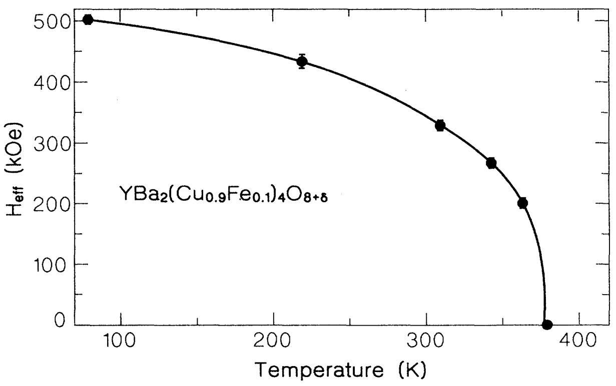

FIG. 4. Temperature dependence of the magnetic hyperfine field acting on ^{57}Fe in Cu(2) sites in $YBa_2(Cu_{0.9}Fe_{0.1})_4O_{8+\delta}$.

$T_N = 110(10)$ K (see Fig. 2) was determined by using a universal experimental curve derived from Fig. 4 in analogy with the universal curve recently proposed for the 1:2:3 system.[15] No magnetic subspectra were observed in the superconducting range where $x < 0.04$. More details on the spectra exhibited in Fig. 3, including Mössbauer spectra obtained at low (4.2 K) and high temperatures will be presented in a forthcoming paper.

Our Mössbauer studies clearly indicate that Fe atoms occupy predominantly the Cu(1) sites, with an increasing fraction of Fe residing in the Cu(2) sites as the total amount of dopant increases. When the Cu(2) planes become magnetically ordered, the Cu ions produce an exchange field at the iron located in the Cu(2) site and none at the iron in the Cu(1) site. The iron nuclei in the Cu(2) site experience a magnetic hyperfine field leading to the sextet pattern in the observed Mössbauer spectra.

In Fig. 2 the change of T_N as a function of x is shown. T_N decreases from 380 K for $x = 0.10$ to 110 K for $x = 0.07$. The superconducting-antiferromagnetic phase diagram exhibited in Fig. 2 for $YBa_2(Cu_{1-x}Fe_x)_4O_{8+\delta}$ is very similar to that obtained for $YBa_2(Cu_{1-y}Fe_y)_3O_7$,[10] $Y_{1-x}Pr_xBa_2Cu_3O_7$,[9] and $YBa_2Cu_3O_z$.[7] All these examples indicate that antiferromagnetism is commonly found at concentrations where superconductivity disappears. The collected evidence indicates that in both 1:2:3 and 1:2:4 systems the competition between superconductivity and magnetism leads to the appearance of one phenomenon whenever the other disappears.

Based on the studies reported here we can summarize the behavior of the $YBa_2(Cu_{1-x}Fe_x)_4O_{8+\delta}$ system as follows:

(i) The orthorhombic structure observed at low x values changes to a tetragonal structure when the Fe concentration is increased.

(ii) Fe doping sharply reduces T_c of the 1:2:4 system. The system is superconducting for $x < 0.04$ but antiferromagnetic at the Cu(2) site for high values of x.

(iii) For low x values, in the region where the 1:2:4 systems exhibit superconductivity, the observed Mössbauer spectra contain a single quadrupole doublet. This indicates that, for low Fe concentrations, Fe predominantly occupies the Cu(1) site.

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